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U.S. PATENT DOCUMENTS

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ABSTRACT

TITLE:

7.184 101.

S Claims, No Drawings

A STORY OF BOLD | Street A SECTION | Pimary Examine.—G. I., Kaplan Attorney, Agent, or Firm.—Birch, Stewart, Kolasch, and Birch An electroplating bath for depositing tin or a tin alloy with articlarity brightness, which comprises a mother beth of a pit-sulte ranging from 4 to 8 and containing cityle acid or its sult, an annonium sat to all a water-sol-wise polymer as a brightnere. The bath may further comprise an aldehyde compound as a co-brightner. FOREIGN PATENT DOCUMENTS 1469547 4/1977 United Kingsdom .... 3,616,306 3,769,182 3,892,637 3,905,878 **E**5 36 52-136730 52-136731 204/45 5; 204/44; 204/54 R 204/44, 120, 123; 106/1,25; 1.22 CASD \$/\$2, CASD 3/60 Shuji Igerachi; Yoshikeza Fujisawa; Toshio Igerachi, ali of Tokyo, Japan Dipped Chemicals Co., Ltd., Tokyo. ELECTROPLATING BATH FOR DEPOSITING TIN OR TIN ALLOY WITH <u>E</u> Foreign Application Priority Data United States Patent Nov. 15, 1978 [21] Appl. No.: 960,944 Japan BRIGHTNESS [38] Field of Search EE Int C.? U.S. C. (garashi et al. Inventors: Assignee: Nov. 16, 1977 [ Nov. 16, 1977 [ Filed T 3 Ē 77 至宽 8 USPAT USPAT USPAT USPAT USBAT USPAT Abstract Text - ABTX (1):

An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and brightness, which comprises a mother bath of a pH-value ranging class of containing cittic acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as phthalic soid anhydride, or adding to the final reaction product an aromatic aldehyde as a co-brightener (Jap. Pat. Appln. No. 149 697/1974 which was early opened under the number of 75 632/1976). The brightener is advantageous in attaining a "bright" or "semi-bright" tin-zinc alloy electroplating regardless of a kind of the metal to be plated or an electroplating bath to be employed. The brightener, however, has a practical disadvantage that the range The present invention relates to an electroplating bath for depositing tin or a tin alloy with brightness, and more particularly to such a bath containing citric acid or its salt and an ammonium salt. Electroplating bath for depositing tin or tin alloy with In the printed specification for said USSR Inventor's Certificate, there is a disclosure that dextrine and gelatine are added as brighteness to attain a finer and crystalline tin-zinc alloy deposition with a brightness. However, the "brightness" to attained by this Inventor's Certificate process is of the degree dull or "mat" among the brightness degrees comprising bright (mirror bright), semi-bright, dull, mat and dendrite. In order to improve the brightness, one of the present inventors has proposed together with others a brightener for timrains alloy electroplatings, which is a water-soluble polymer obtained by reacting an aliphatic amine with an organic acid ester and then further reacting the reaction product with Brief Summary Text - BSTX (9):
A specific object of the present invention is to provide an electroplating Kind Codes In order to overcome the disadvantages as referred to, a bath containing citric acid or its salt and an ammonium salt has been proposed (see, for instance, USSR Inventor's Certificate No. 293,876). working current density required during the electroplating is relatively D. ם ם u u us 4168223 A brightness ш Document ID v Pages 1 L ш 4168223 Brief Summary Text - BSTX (1): Brief Summary Text - BSTX (6): Brief Summary Text - BSTX (5): Brief Summary Text - BSTX (7): 01 10 6 2 DOCUMENT-IDENTIFIER: US 4428803 A US 4401526 A US 4299671 A us 4488942 A us 4290860 A US 4168223 A a co-brightener. US-PAT-NO:

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22 vs 4877494 A 36 C C C C C C C C C C C C C C C C C C	[54] ELECTROPLATING BATHS, ADDITIVES THEETHODS FOR THE	Primary Examiner—G. L. Kaplan Attorney, Agent, or Flym—Maky, Remuer, Otto &
24 US 4801368 A 10 T C C C F C F		Boisselle
	[75] Inventor: William E. Eckler, Cleveland Heights, Ohio	[57] ABSTRACT Bright level metal denosits can be obtained on sub-
	[73] Assignee: McCests-Robco, Inc., Cleveland, Ohio	
W3-PAT-NO: 4384930	[21] Appl. No.: 294,976	least one surfactant of the formula
DOCUMENT-IDENTIFIER: US 4384930 A		ROCH,CH(CH)OCH,CH(CH)NRH)CH,CH. 5COOH
TITLE: Riectroplating baths, additives therefor and methods for the electrodeposition of metals	[51] Int. Cl. <sup>3</sup>	ı
**************************************	204/50 R; 204/52 R; 204	ROCH2CH(CH))OCH2CH(CH))N
	[38] Flets of Search	, (CH2CH2O),
Abstract Text - ABTX (1): Bight level metal deposits can be obtained on substrates from aqueous	K, 30, 1, 31, 32, K, 32, Y, 33, 34, K, 34, L, 55, K, 55, X, 35, X, 43, K, 43, Z, 43, G, 43, S, 47, H, 13, K, 43, P, 44, D)G. 2	wherein R is an alkyl group containing 10 to 12 carbon atoms, x and y are integers, the sum of which is from 2
at least one <u>surfactant</u> of the formula	[56] References Cited	to moout A. 1 he squotants and paramage carries or the in- ternation will preferably contain as a brighteening agent, at feast one carbonyl-containing compound. These plate
Brief Summary Text - BSTX (3): The electrodenosition of matals from announs solutions of the enterly inter-	U.S. PATENT DOCUMENTS 4.13,991 1/1979 Caparis et al	ing baths exhibit low fourning characteristics.
well known. The present invention is concerned particularly with equeous acid electroplating baths for depositing metals such as tin, lead, copper, zinc,		
cadmium or Lin-lead mixtures. The composition of the metal electroplating bath will be determined at least in part by the particular metal to be a least in the bath the particular metal to be a least in the least		
improving the effectiveness of electroplating baths containing various metals.		
Brief Summary Text - BSTX (4):  In acidic electroplating baths, it is conventional to utilize a surfactant		
therein to control properties of the metal deposit and to assist in solubilizing other organic components. A wide variety of compositions have		
been suggested as surfactants in acid electroplating baths, and many of these are commercially available polysthylene oxide-based materials, and, therefore, tryically contain a hydronhilic and hydronhilic and successions.		
structure.		
Brief Summary Text - BSTX (5):  The present invention is directed narticularly to improved excess saiding		
plating baths for depositing tin and/or lead coatings. Generally, these plating baths contain, in addition to the water-soluble tin and/or lead salts,		
at least one group selected from the group consisting of fluoborates, fluosilicates, sulfametes, etc. In addition to these basic	•	
including additives which will improve the brightness of the deposit obtained from such baths by		
monocarboxyaldehyde either alone or in combination with certain substituted		
the deposit. Other ingredients which have been suggested as being useful additives in the analyst last the heart which have been suggested as being useful.		
carbonyl-containing compounds such as-eldenydes, ketones and carboxylic acids, etc. For example, U.S. pat No. 1745 A40 Associates the advantage of the carboxylic acids,		
izing tin-lead plating baths containing at least one arematic surfacetant		
is described ir		٠

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#### Ξ United States Patent Kurze et al,

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4,820,388 Apr. 11, 1989

Patent Number: Date of Patent:

### POLYALKYLENE GLYCOL NAPHTHYA-SULPOPROPYL DIETHER COMPOUNDS AND THERE SALTS, PROCESS FOR PREPARING SAME AND ELECTROPLATING BATHS CONTAINING <u>\*</u>

USPAT

Werner Kurze, Neubofen; Klaus-Peter Klas, Trebur, both of Fed. Rep. of Germany Inventoris: 3

: Reschig AG, Ludwigalasfen; Elekro-Brite Gabh & Ca. KG, Trebur, both of Fed. Rep. of Germany; a part interest [73] Assignees:

[21] Appl. No.: 205,631

Jun. 13, 1988 Filed: <u>B</u>

Jul. 9, 1987 [DE] Fed. Rep. of Germany ...... 3722778 Foreign Application Priority Data

III Q 至 [32]

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4,133,375 5/1979 Kalfogiou et al ....... 260/512 CX Novel Polyaltylenglycol naphthyl-3-sulfopropyl dieth-en and salts thereof of the formula Primary Examiner—G. L. Kapian Attorney, Agent, sv Firm—Collard, Roe & Gelgano U.S. PATENT DOCUMENTS References Cited ABSTRACT 3

O-A-CH2-CH2-CH2-5038

(R.-R.)=H, C.H., p=1—4, A=(PO), —(EO), — (EO), —(PO), EO=ethylenoxide residue, PO=propylenoxide residue, A=H, alkali meni, earth aitheil meni, NR, R.R. Puberion, R.-R. EH, C.-C.—alkyl, aryl, sanlayl) are prepared by reacting the corresponding polyalkylene siven maptityl either with proparel.1-sanlane. The compounds are surfactants in particular in electroplatic ing baths for precipitation Zn, Sp, Cu, Ag, NI and alloys thereof.

7 Claims, No Drawings

Brief Summary Text - BSTX (13): The amounts of the compounds of the invention to be used in electroplating

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US-PG [0011] It has been surprisingly found that tin or tin-alloy may be uniformly deposited over a wide current density range using the electrolyte compositions of the present invention. It has been further suprisingly found that the electrolyte compositions of the present invention plate tin or tin-alloy at high current densities with low metal concentrations, while producing a uniform tin-alloys over a wide current density range while maintaining a uniform deposit appearance over the current density range, particularly for use in high speed plating systems. [0012] In one aspect, the present invention provides an electrolyte composition [0013] In another aspect, the present invention provides a method for depositing tin or tin-alloy on a substrate including the steps of contacting the substrate with the electrolyte composition described above and applying a sufficient current density to the electrolyte composition to deposit the tin or lyet another aspect, the present invention provides a substrate having tin-alloy deposited thereon according to the method described above. [0016] In a still further aspect, the present invention provides a method for high speed electroplating of tin or tin-alloys including the steps of: a) utilizing high speed electroplating equipment comprising an electroplating cell; an overflow reservoir adjacent the cell; means for returning solution from the reservoir to the electroplating cell; means for directing a substrate to be plated from an entry point at one end of the cell to an exit at a second end of the cell; b) introducing an electrolyte including a basis solution of C P Kind Codes [0010] There is a continuing need for plating baths that will deposit tin or for depositing tin or tin-alloy on a substrate, including one or more tin compounds, one or more acidic electrolytes, and one or more carboxyalkylated composition for depositing tin-copper alloy on a substrate, including one or more tin compounds, one or more copper compounds, one or more acidic electrolytes, and one or more carboxyalkylated polyalkyleneimine compounds. [0008] Certain polyalkyleneimines are known for use in zinc electroplating baths. See, for example, German Pattert Application BS 3121016. Such polyalkyleneimines may be substituted with carbamoyl and/or thiocarbamoyl groups. The use of polyalkyleneimines is not disclosed for use in <u>Ein or</u> the present invention provides an electrolyte No. 5,282,954 (Opaskar) discloses alkoxylated diamine Carboxyalkylated er - L11; (45) 6 and 10 I US 20020187355 At 1 Tag: 5 I Doc; 38/45 (SORTED) I Format ; FUL П L deposit appearance over the entire current density range. ÞΣ ĺΣ Σ <u>surfactants</u> for use in tin electroplating baths. Ca polyalkyleneimines are not disclosed in this patent. Ц U U П u u u Ľ Document ID v Pages 1 Ľ ш ш polyalkyleneimine compounds [0015] In a further aspect, tin-alloy on the substrate US 20030168341 A 14 US 20030150743 A 12 US 20030141192 A 14 US 20030066756 A 12 SUMMARY OF THE INVENTION tin-alloy plating baths. US 20030070933 A 5 US 20020187364 A 6 US 20020187355 A 8 [0014] In yet another [0009] U.S. Pat. tin or 3. EAST Bro Ŧ 

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Electrolyte compositions for the deposition of tin and tin-alloys on a substrate are disclosed, along with methods of electroplating tin and tin-alloys using such compositions. These electrolyte compositions are useful for high good tin 0112599.6 0112769.5 ... C25D 3/60; B32B 15/00 . 428/432; 205/252; 205/300 (10) Pub. No.: US 2002/0187355 A1 Dec. 12, 2002 Foreign Application Priority Data Publication Classification ABSTRACT (43) Pub. Date: 99 May 24, 2001 May 25, 2001 Ē.Ω., U.S. Ω. (52) (52) Patent Application Publication S. Matthew Cairns

olo EDWARDS & ANGELL, LLP

Dike, Bronstein, Roberts & Cushman, IP Group Assignee: Shipley Company, L.L.C., Marlbor-Inventor: Jeffrey N. Crosby, Warwickshire (GB) May 6, 2002 10/139,562 P.O. Box 9169 Boston, MA 02209 (US) Correspondence Address: ough, MA TIN PLATING Appl. No.: Crosby Filed: **₹** 3 દ <u>a</u> 8 Ê US-PG US-PG US-PG-US-PG

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invention provides a mathod of

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our puryarkytates polyalkyleneimine compounds; and c) continuously electroplating substrates with tin or tin-alloy at a sufficient current density and at a sufficient temperature for high speed electroplating as the substrates pass through the electroplating solution within the cell.

one or more tin compounds, one or more acidic electrolytes, and one or more carboxyalkylated polyalkyleneimine compounds; and c) continuously

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(0035) The plating bath of the present invention may nonionic surface active agent if necessary.	9. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4. 4.	и в ц	ent	inv	ent.	ä	nay k	be in	corpo	incorporated with a	
[0036] A nonionic) surface active agent helps the Sn-smooth delise-sufface and with a uniform composition.	ive	p a	fort	hel		the	- 18 - 16	Cu al	loy d	SnCu alloy deposition with on. It should preferably he	ø
one which is derived-from alkylene oxide. It includes, for exc pp. Joynychelline bette, nephthol ether ethylene oxide-propylene oxide-propylen	켔밁	함	3/6\	eth	y It	ing o	It includes,	prop	r exe ylene	ethylene oxide-propylene oxide block	
polyoxyethylene alkylamino et polyoxyethylene polyhydric al	ether,	9,4	olyoxy ether,	xya r,	thy]	ene. pol,	ether, polyoxyethylene fatty aci alcohol ether, and polyethylene	y ac	posty, ecre acid ester, ne alycol.	ecier, iter, ol. Its amount	ע
	t efe	rab. higi	Ly b	e i	01-	50 c		part f it	particularly if its amount	2-10 g/L.	ä
excessively small, and it may cause the plating fill or uneven color if its amount is excessively large.	Q	e X	cause the plating is excessively lan	r. pl	tir ly 1	ام الم ام الم	Ę	to as	a s s um e	a blackish color	Ä
[0037] The plating bath of the present invention may be incorporated with or more of cationic <u>surface active agents</u> , anjonic <u>surface active agents</u> , amphoteric <u>surface active agents</u> , if necessary	orti p	9 5 7	ant agen	inv	enti eni sery	unite .	any b	face face	ntion may be incorporatenionic surface active	rated with one ve agents, and	
[0038] Examples of the cationic surface active agents include dodecy ammonium salt, hexadecyltrimethyl ammonium salt, octodecyltrimethyl	thy	Sur.	face	a c	ci ve	t,	surface active agents l emmonium salt, octad	incl	nde d trime	include dodecyltrimethyl ecyltrimethyl ammonium	_
salt, dodecyldimethylethyl ammonium salt, octadecenyldimethylethyl salt, dodecyldimethyl ammonium betains, octadecyldimethyl ammonium dimethylbenzyldodecyl ammonium salt, hexadecyldimethylbenzyldomennyn	H H H	ium etej elt,	sel ne,	xade	octs tade	dece	enyld limet	imet hyl henz	octadecenyldimethylethyl tadecyldimethyl ammonium ecyldimethylbenzyl ammoni	nium selt, octadecenyldimethylethyl ammonium betaine, octadecyldimethyl ammonium betaine, selt, hexadecyldimethylbenzyl ammonium selt	
octadecyldimethylbenzyl ammonium salt, triethylbenzyl ammonium salt, hexadecyl	he	se.	t,	tri	neth iidi	ylbe	nzyl		trimethylbenzyl ammonium pyridinium salt, dodecyl	monium salt, dodecyl pyridinium	
salt, dodecyl picolinium salt, dodecyl imidazolium salt, salt, octadecylamine acetate, and dodecylamine acetate.	មិន្តិ	g g	y, dec	yler.	in ne	lium ace	dodecyl imidezolium salt		oleyl	imidezolium	
[0039] Examples of the (anionic) surface active agents include alkyl sulfate, polyoxyethylene alkyl ether sulfate, [polyoxyethylene-alkylphenyl ether sulfate, and (not) alkylphenylenesulfonate.	035	urfe ate,	9 8 5	Lyo.		ager hyle	ne te	nclu Eyij	le al	kyl sulfate,	G
ary two soliosurioses, ask (pory) arkyrnaphthar alkyl sulfonate include sodium dedecylsulfate	o d	ad et	, y.r.ı ; y.l.s	4	cha.	ene	urro sodi	ulionate sodium oleyl	ev1	Examples of the sulfate.	_

the <u>(nionic) surface active agents</u> include alkyl sulfate.

1. ether sulfate, <u>polyozychylene-alkyphinal erhat sulfate</u>,

2. and (poly) alkylnaphthalensaulfonate.

2. and dedecylsulfate and sodium oleyl sulfate. Examples of the polyoxyethylene alkyl ether sulfate include sodium polyoxyethylene (BO12) nonyl ether sulfate and sodium polyoxyethylene (BO15) dodecyl ether sulfate.

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[0040] Examples of the amphoteric surface active agents include betaine, sulfobetaine, and imidazolium betaine. Additional examples include sulfated adduct or sulfonated adduct of a condensation product of ethylene oxide and/or propylene oxide with alkylamine or diamine.

[0041] The amount of these surface active agents in the plating bath should preferably be 0-50 g/L, preferably 0.01-50 g/L, particularly 2-10 g/L.

[0042] The plating bath of the present invention may be incorporated with one or more of mercapto group-containing arcmatic compounds, dioxyarcmatic compounds, and unsatureted carboxylic acid compounds, as a leveling agent for the plating film and an antioxident for 9n. sup.2+ion in the plating beth. Examples of the mercapto group-containing arcmatic compounds include 2-mercaptobenzoic acid, mercaptophenol, 2-mercaptobenzoxazole,

United States 6

(12) Patent Application Publication (10) Pub. No.: US 2002/0104763 A1 Aug. 8, 2002 (43) Pub. Date: YANADA et al

TIN · COPPER ALLOY ELECTROPLATING BATH AND PLATING PROCESS THEREWITH <u></u>

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IS BAMU YANADA, HIRAKATA,SHI (IP); MASANOBU TSUJIMOTO, HIRAKATA,SHI (IP); TETSUROU OKADA, HIRAKATA,SHI (IP); TERUYA OKA, HIRAKATA,SHI (IP); HIDEYUKI TSUBOKURA, Inventors:

SUGHRUE MION ZINN MACFEAK & SEAS 2100 PENNSYLVANIA AVENUE NW WASHINGTON, DC 200373202 HIRAKATA-SHI (JP)

Notice: ε

09/433,887

(21) Appl. No.:

This is a publication of a continued prosecution application (CPA) filed under 37 CFR 1.53(d).

ABSTRACT in Cl. U.S. Cl.

Publication Classification

EE

Nov. 5, 1998 May 7, 1999

11-127648

Foreign Application Priority Data

Nov. 4, 1999

Filed g 8 A tin-copper alloy electroplating bath which comprises a water-soluble in salt, a water-soluble copper salt, an inorsible to form a in-copper aloy deposit, in place of the-lead alboy plating, on electronic parts such as chips, quartz crystal oscillators, hoops, connector pins, lead frames, bumps, lead pins of packages, and printed circuit boards. game or organic acid or a water-soluble salt thereof, and one or more compounds selected from thiosmide compounds and third compounds. The present invention makes it pos-

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er - L11: (45) 6 and 10 LUS 6582582 82 LT ag: S LD ac: 2/45 (SDRTED) | Format : KWIC us 6582582 B2 us 6562221 B2 US 6562220 BZ US 6508927 BZ us 6500886 B1 US 6478944 B1 US RE29239 **※** ± ↓↑ ₹ ¶ ፟ Ø OEG

bath upon make-up with a soluble source of zinc ions such as zinc sulfate or zinc chloride. Stannous sulfate and zinc sulfate are preferred sources of tin and zinc ions respectively. Preferably, if present, the concentration of tin ions in the electroplating bath range from about 30 to 50 g/l, most preferably if present, the concentration of zinc ions in the electroplating bath range from about 15 to 40 g/l, most preferably from about 20 to 35 g/l. As noted the electroplating composition is particularly about 20 to 35 g/l. As noted the electroplating composition is particularly electroplating composition. effective in plating tin-zinc alloys. In this case, the electroplating bath comprises both tin and zinc ions and the concentration of tin ions preferably ranges from about 30 to 40 g/l while the concentration of zinc ions ranges from about 20 to 40 g/l.

Brief Summary Text - BSTX (22):

Other known leveling agents and co-brighteners may optionally also be added to the alectroplating bath. These additional optional additives include polyethylene glycols, water soluble polypropylene oxide polymers; water soluble polypropylene oxide polymers, water soluble polypropylene oxide polymers, brightened emines, and various surfactants. Many of the foregoing compounds are polyglycerines, and various surfactants. Many of the foregoing compounds are useful in providing leveling effects and in otherwise brightening the electroplated deposits. The specific compound to be salected depends upon the specific electroplating bath but the inventor has found the following compounds to be particularly useful in tin, zinc, or tin-zinc electroplating baths:

It used, the concentration of these leveling agents and co-brighteners may range from about 0.5 to 5 g/l in the electroplating bath. 

Brief Summary Text - BSTX (25):

As noted, the electroplating bath of this invention is particularly suited to plating tin-zinc alloy electrodeposits. Electrodeposits of approximately 75% tin and 25% zinc are widely used in industry in improving the corrosion resistance of steel substrates. An elemplary formulation for producing 75/25 tin-zinc electrodeposits is as follows:

Brief Summary Text - BSTX (26);

smooth electrodeposits over steel substrates. In this case the cathode would be a steel substrate and the anode would consist of a combination of the and The inventor has found that the foregoing formulation is capable of delivering a 75/25 tin-zinc alloy (.+.5%) electrodeposit over a plating current density range of 50 to 300 amps per square foot (ASP) with bright, zinc substrates.

Brief Summary Paragraph Table - BSTL (1);

Component Concentration Stannous Sulfate 30-50 g/l (as tin) Zinc Sulfate 20-40 g/l (as zinc) Citric Acid 25-150 g/l Ammonium Sulfate 50-150 g/l propanedioic acid diethyl ester polymer 0.5-1.5 g/l with N- $(3-\mathrm{aminopropyl})_1,3-\mathrm{propanedioin}$  N- $(2-\mathrm{carboxybearcyl})$  Diglycidyl Polyethylene Glycol 0.5-1.5 g/l Veratryl aldehyde 0.05-0.5 g/l

Detailed

.ailed Description Text - DETX (2): The following  $\frac{1}{1}$  in electroplating bath was formulated:

#### United States Patent Becking 3

US 6,582,582 B2 Jun. 24, 2003 (45) Date of Patent: (10) Patent No.:

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Technical Bulletin, DGV SZ-240 & DGV SZ-242, TinZinc Plating Process, Dipsol Gumm Ventures. No date Fin/Zinc Alloy Plating, Jean Rasmussen, Plating & Surface

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 174 days.

Donald Becking, 138 Tanglewood Dr., Southington, CT (US) 06489

(54) ELECTROPLATING COMPOSITION AND

PROCESS

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Pages 1 3

Inventor:

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(\*) Notice:

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Battas, S.M. Abdel-Wahab, et al., Metall, May 2000, pp
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Tin-Zinc Flating, Edward Budman, Dipsol Gumm Vertures and David Stevens, Advance Surface Treatments, U.K. M. An et al., Flating & Surface Finishing, May 1999, pp 1998, No month avail.

205/261; 106/1.25; 106/1.16; 106/1.29

C25D 3/56

Prior Publication Data

Mar. 9, 2001

Filed

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Appl. No.: 09/803,631

US 2002/0170828 A1 Nov. 21, 2002

Int. Cl.7 U.S. C.I.

52 (52

Inventory Expert Service Report, Registry No. 301539-72-0, Propanedioic acid, American Chemical Soci. aty. No date available,

cited by examiner

(58) Field of Search

(74) Attorney, Agent, or Firm-Carmody & Torrance LLP Primary Examiner—Roy King Assistant Examiner—Wesley A. Nixolas

#### ABSTRACT દ

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young in a smooth and bright electrodeposit. The disclosed electroplating bath comprises propanedicic acid, diethyl ester, polymer with N-(3-aminopropyl)-1,3-propanediamine, N-(2-carboxy benzoyl) as a brightener additive. In addition, the electroplating bath may also com-An electroplating bath is disclosed that is particularly suited to the electrodeposition of tin, zinc and alloys of the foreprise carboxylic scids, ammonium salts, aldehyde comcounds and a variety of co-brighteners.

> 205/253 205/252

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Saburei et al.

32 Clatins, No Drawings

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C P Kind Codes		C C C C C C C C C C C C C C C C C C C	(21) Appl No.: 09/965,743 OTHER PUBLICATIONS omposition for high speed plating of tin (22) Fied: Sep. 28, 2001 F.A. Lowenbein, Electroplating, McGraw-Hill Bc (65) Prior Publication Data New York, pp 389-391, 1978.*	(51) Int. Cl. <sup>7</sup> C250 343 (52) U.S. Cl. 205754; 205/140, 205/302; 205/303 (58) Field of Search 205/303, 205/303 205/203, 205/303, 204, 302, 303, 304; 106/1.22, 1.25	(56) References Cited close of the foregoing metals such as nickel.  U.S. PATENT DOCUMENTS ammonime in the such and a source of ammonime in the such as a such	the Ass	
		□ ; BB ; □ :	DOCUMENT-IDENTIFIER: US 6562221 B2 TITLE: and tin alloys	Brief Summary Text - BSTX (19):  The plating composition may be used to plate tin or tin alloys. If tin alloy plating is desired then the plating composition should also comprise a source of metal ions corresponding to the alloying element(s). Suitable alloying elements include zinc. lead. concer. hismuth and nickel. If allow	the foregring me, bismuth sulfate entration of the ing upon the allo	Brief Summary Text - BSTX (21):  The plating composition may also preferably comprise known plating performance additives such as those described in U. 9. Pat. No. 6,217,738, teachings of which are incorporated by reference herein in their enrirety. disclosed therein these plating performance additives may include certain mono. dioc tri-substituted phenols. These substituted phenols may have at least one substituted phenols. These substituted phenols are secondary, tertiary, or properties of the plate and are said to improve the appearance and physics properties of the plate and the overall plating performance of the process, and/or water soluble polymers may also be employed as plating performance additives. Preferably the concentration of plating performance additives in the plating composition will range from about 0.5 to 20 g/l.	Current US Original Classification - CCOR (1): 205/254

(12) United States Patent Gillman et al. USPAT USPAT Kind Codes

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US 6,562,220 B2 \*May 13, 2003 (45) Date of Patent: (10) Patent No.:

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Metal alloy sulfate electroplating baths

ammonium salts of alkyl and alkanol sulfonic acids as additives in pure metal and metal alloy sulfate electroplating baths has a number of unexpected benefits including wider useful current density range, improved appearance and in the case of tin improved oxidetive stability. The metals and alloys include but are not limited to tin, nickel, copper, chromium, cadmium, iron, rhodium, ruthenium, iron, zinc and tin/zinc. ammonium and substituted Abstract Text - ABTX (1): The use of alkali metal, alkaline earth metal,

Brief Summary Text - BSTX (8):

It is therefore worthwhile to identify other additives that can improve the performance of metal sulfate electroplating baths. There are many examples in the prior art where surfacetants and other organic additives are used to provide a more desirable finish. In the case of tin the prior art also describes additives which can improve the oxidative stability of the tin and therefore provide a bath with less sludge formation. It is less common to find examples of additives which improve the plating range especially at the high current density end. Increasing the current density is a very desirable feature but it has been difficult to identify additives which can do this without creating other problems in the bath.

Brief Summery Text - BSTX (14):

The baths that can be improved by the present invention include tin and tin alloys, nickel and nickel alloys, copper and copper alloys, chromium and chromium alloys, teamium and cadmium alloys, iron and iron alloys, ruthenium and ruthenium alloys, and especially the iron/zinc tin/zinc alloy plating baths.

Brief Summary Text - BSTX (20):

Typical additives include a surfactant such as an ethoxylated fatty alcohol, a brightening agent if required and an antioxidant such as hydroquinone or any These baths also contain the corresponding metal salt or metal salts if alloy plate is required, and various additives to control the quality and appearance of the plated surface and the stability of the bath solution. catechol, if tin is one of the metals being plated.

Detailed Description Paragraph Table - DETL (1):

Bath Composition: 5% Sulfuric Acid 20.0 g/l Sn (as stannous sulfate) 3
g/l JWL 5000 surfactant 0.1 g/l salicylic acid Bath base 5 ppm 2.9 - Dimethyl phenathroline Rum # Additive and Level Results of Plating Tests 1 No additive Dark burn on high current density edge at 5 Amps. Burn is 12 mm wide at high current density edge at 10 Amps. 2 10 g/l Sodium isethionte Even light gray satin deposit at (calculated as isethionic acid) 10 Amps - no burn.

### METAL ALLOY SULFATE ELECTROPLATING BATHS (34)

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(US), Brends Fernandes, Cranson, RI (US), Kazimierz Wikiel, Wakcheld, Ri (US) Hyman D. Gillman, Spring City, 1 Inventors: ନ

USPAT

Technic, Inc., Cranston, RI (US) Assignee: Ē

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 74 days. ( \* ) Notice:

This parent is subject to a terminal dis-

Appl. No.: 09/862,166

May 21, 2001 Filed: 8 Prior Publication Data 8

Related U.S. Application Data US 2002/0014414 A1 Feb. 7, 2002

Continuation-in-part of application No. 09/272,800, filed on Mar. 19, 1999, now Pat. No. 6,251,253. 3

Cl. 205/244; 205/245; 205/246; 205/244; 205/244; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; Int. CL, ...... U.S. C. 

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(74) Attorney, Agent, or Firm-Ernest V. Linek; Banner & Primary Examiner-Kishor Mayekar Witcoff, Ltd.

ABSTRACT

acids as additives in pure metal and metal alloy sulfate electroplating baths has a mimber of unexpected benefits appearance and in the case of tin improved oxidative sta-bility. The metals and alloys include but are not limited to The use of alkali metal, alkaline earth metal, ammonium and substituted ammonium salts of alkyl and alkanol sulfonio tin, nickel, copper, chronium, cadmium, iron, rhodium, ruthenium, iron/zinc and tin/zinc. including wider useful current density range, improved

31 Claims, No Drawings

Brief Summary Text - BSTX (52):
The plating bath of the present invention may be applied to rack plating,
barrel clating, or high-speed clating, in the usual way. The cathode current
barrel clating, or high-speed clating in the usual way. The cathode current

ASIMI ST Bloome Brown Brown Action Bloome Bloome Brown Bro ଞ £88 USPAT USPAT USPAT USPAT USPAID USPAT Examples of the anionic surface active agents include alkyl sulfate, polyoxypthylene alkyl ether sulfate, polyoxypthylene alkyl ether sulfate, alkylnaphthalenesulfonate. Examples of the alkyl sulfonate include sodium dedecylsulfate and sodium oleyl sulfate. Examples of the polyoxypthylene alkyl ether sulfate include sodium polyoxypthylene alkyl ether sulfate include sodium polyoxypthylene (E015) The plating bath of the present invention may preferably be incorporated with one or more of water-soluble metal salts selected from water-soluble gold salts, water-soluble silver salts, water-soluble bismus salts, water-soluble constants, water-soluble bismus salts, water-soluble cobalt salts, and salts, and can form a dense termary alloy of Sn-Cu-Au, Ag, Zn, Bi, Ni, Co or Ed due to the codeposition of the metal (Au, Ag, Zn, Bi, Ni, Co or Pd) with Sn and Cu, or the water-soluble metal salt can act as an additive for forming a dense deposit, improving a solderability, and preventing the deposit from discoloring Examples of the amphoteric surface active agents include betaine, sulfabetaine, and imidezolium betaine. Additional examples include sulfated adduct or sulfanated adduct of a condensation product of ethylene oxide and/or ö Brief Summary Text - BSTX (41):
Examples of the cationic surface active agents include dodecyltrimethyl ammonium salt, hexadecyltrimethyl ammonium salt, octadecyltrimethyl ammonium salt, dodecyldimethylethyl ammonium salt, dodecyldimethylethyl ammonium dimethylbenzyldodecyl ammonium salt, hexadecyldimethylbenzyl ammonium salt, octedecyldimethylbenzyl ammonium salt, trimethylbenzyl ammonium salt, triethylbenzyl ammonium salt, hexadecyl pyridinium salt, dodecyl pyridinium salt, dodecyl pyridinium salt, asslt, olectyl pyridinium salt, all imidazolium salt, olethyl imidazolium salt, olethylamine acetate, and dodecylamine acetate. The plating bath of the present invention may be incorporated with one of cationic surface active agents, and amphoteric) surface active agents, and amphoteric) surface active agents, if necessary. salt, dodecyldimethyl ammonium betaine, octadecyldimethyl ammonium betaine, The amount of these surface active agents in the plating bath should preferably be 0-50 g/L, preferably 0.01-50 g/L, particularly 2-10 g/L. Ш ser - L11; [45] 6 and 10 LUS 6508927 B2 LTag: S I Doc; 5/45 (SORTED) I Format; KWIC octadecylamine acetate, and dodecylamine acetate. 12 ĺΣ ĽΣ D. Σ u L propylene oxide with alkylamine or diamine. L U U u Document, ID v Pages 1 Ľ Brief Summery Text - BSTX (40): Brief Summary Text - BSTX (43); Brief Summary Text - BSTX (42): Brief Summary Text - BSTX (44): Brief Summary Text - BSTX (47): 13 dodecyl ether sulfate. after heat treatment. US 6582582 B2 us 6562221 B2 US 6508927 B2 us 6500886 B1 us 6562220 BZ US 6478944 B1 US RE29239 E ②歐額 ※ 中 

#### United States Patent Yanada et al. 3

#### US 6,508,927 B2 \*Jan. 21, 2003 (45) Date of Patent: (10) Patent No.:

# (54) TIN-COPPER ALLOY ELECTROPLATING

### Masanobu Tsujimoto, Hirakata (1P); Tetsurou Okada, Hirakata (1P); Teruya Oka, Hirakata (1P); Hideyuki Tsubokura, Hirakata (1P) Isamu Yanada, Hirakata (JP); (75) Inventors:

### C. Uyemura & Co., Ltd., Oseka (IP) (73) Assignee:

### This patent issued on a continued mos-ecution application filed under 37 CFR ecution application filed under 37 CFR 1.53(d), and is subject to the twenty year patent term provisions of 35 U.S.C. ( \* ) Notice:

J. Horacon . I Nork! W.Y.

## Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

09/433,887	
No.:	
Appl.	
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#### Prior Publication Data US 2002/0104763 A1 Aug. 8, 2002

### Foreign Application Priority Data 8

## 19 Claims, No Drawings

205/241, 253,

Field of Search

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Assistant Examiner—Wesley A. Nicolus (74) Attorney, Agent, or Firm—Sughrue Mion, PLLC Primary Examiner—Nam Nguyen

### ABSTRACT

and thiol compounds. The present invention makes it pos-sible to form a five-toper alloy deposit, in place of the lead alloy plating, on electronic parts such as chips, quartz crystal oscillators, boops, connector pins, lead france, bumps, lead water-soluble in sait, a water-soluble copper sait, an inor-ganc or organic soid or a water-soluble sait theroof, and one A tin-copper alloy electroplating bath which comprises a or more compounds selected from thioamide compounds pins of packages, and printed circuit boards.

ser - Lili: (45) 6 and 10 LUS 6500886 BIITag: \$1 Doc: 6/45 (SORTED) | Format : KWIC 23: EAST Brow

USPAT USPAT USPAT USPAT USPAT USPAT ĺΣ ĽΣ 2 ĺΣ ĺΣ lΣ Σ נו L L L ם Ш L 11 13 'n US 6500886 B1 us 6478944 B1 US 6582582 BZ US 6562221 B2 us 6562220 B2 us 6508927 B2 US RE29239

alkali metals, alkaline earth metals, transition metals, polyethylene waxes, dyes, alcohols, and resins; and combinations with at least one of resins, conductivity-imparting agents, pigments, torque adjusting agents, alcohols, and These is no special limitation to the sources of the above substances to be supplied. Various sources may be used, including metal sulfates, nitrates, hydrochlorides, and other salts, silicate compounds, silan design quality, impartment of electric conductivity, and control of friction compounds, oxy-acid salts, complex salts, nitrides, oxides, and sulfites. Examples of these combinations are combinations of Si and at least one of torque coefficients). ethers. ğ

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Detailed Description Text - DETX (53):

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Plating was carried out using zinc as the anode, with a solution (pH 4) which contained, all per liter, 288 g white vitriol, 25 g boric acid, 27 g ammonium chloride, 50 g of fine silica powder having a particle diameter of 18 m.m. ("Bitaseal #1500" made by Taki Sahih K.K.), 0.001 min nonlonic surfactant (polyoxyethylemelaurylamine), and 0.0005 M cationic surfactant (dodecyltrimethylamine), and 0.0005 M cationic surfactant which had been suspended Thus a plating layer about 5. mu.m. thick was formed on the side A of test specimens. Partial holidays had occurred at that point. Test specimen A. Another specimen was immersed for 60 seconds in a treating solution which contained, all per liter, 3 g chromium acetate, 0.1 g sulfuric acid, 0.1 g nitric acid, and 2 g phosphoric acid to obtain Test specimen B. Another specimen was treated in the same way as B and was further immersed for 20 seconds in a treating solution which contained, all per liter, 60 g sodium silicate, 10 g sodium hydroxide, and 0.04 g zinc to obtain Test specimen C. One test specimen was immersed for 35 seconds in a treating solution which contained, all per liter, 5 g ammonium molybdate, 15 g phosphoric acid, 2 g titanium sulfate, 3 g hydrogen peroxide, and 15 g colloidal silica to obtain

Claims Text - CLTX (2):

from 40 g to 300 g caustic alkali, from 0.01 g to 50 g adsorbent, from 0.002 g to 100 g caustic alkali, from 0.01 g to 50 g adsorbent, from 0.002 g to 10 g iron, from 0.002 g to 10 g cobalt, from 0.05 g to 30 g manganese, from 0.001 g to 2 g copper, from 0.005 g to 10 g mickel, from e.002 g to 3 g of at least one member selected from the group consisting of molyhdenum, turngaten, vanadium, titanium, aluminum, calcium, barium, and tin, and from 0.01 to 30 g aliphatic amine or aliphatic amine polymer.

Current US Cross Reference Classification - CCXR (1): 205/244

8 Classification Reference Cross Current UB ( 205/245 Current US Cross Reference Classification - CCXR (3): 205/246

**8 8** 0

United States Patent Yamamuro et al. (12)

US 6,500,886 B1 Dec. 31, 2002 (45) Date of Patent: (10) Patent No.:

> SURFACE TREATING AGENT £9

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Inventors: Masaaki Yamamuro, Tokyo (JP); Mitsuami Katori, Tokyo (JP) 3

Nihon Hyomen Kagaku Kabushiki Kalaha, Tokyo (JP) Assignee: E

Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 54 days. Notice: €

Appl. No.: 09/710,400 a

Nov. 9, 2000 Filed: 8

Foreign Application Priority Data 8

... 11-319339 COSK 5/34; C25D 3/56 9 Int. Ci., Nov. 10, 1999 (£)

**524/99**; 524/440; 205/244; 205/245; 205/246 205/246; 524/99, 440 (58) Field of Search

US. C.

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Primary Examiner—Edward J. Cain (74) Attorney, Agest, or Firm—Marshall, Gesstein & Borun

ABSTRACT

Aplating solution containing zinc, an electrically conductive sail, an adsorbent, and at least one of mono- to hexavalent metal ions. A treament using either a solution which contains, all per libra, 2-60 g Zn, 40-300 g caustic aliesi, 0.01-50 g adsorbent, 0.002-10 g Fe, 0.002-10 g Co, 0.003-90 g at least one choica from among Mo, W, V, Ti, Al, Ca, Ba, and Sn, and 0.01-30 g aliphatic amine or aliphatic amine of Zn, 40-10 g caustic alkeli, 0.01-50, g adsorbent, either 0.001-3 g Fe and 0.003-3 g Co or 0.005-5 g Fe and 0.003-3 g Co or 0.005-5 g Fe and 0.003-5 g N, and 0.01-30 g aliphatic amine or aliphatic amine

20 Claims, 1 Drawing Sheet

The aqueous solution of the invention for the reductive deposition of metals phenyl ether phosphates, polyoxythylene alkyl ether acetates, alkanoyl sarcosinates, alkanoyl sarcosinates, alkanoyl methylalanine salts, alkyl sulfoscetates, acyl methyl tautines, alkyl fatty edig glycerin sulfuric esters, hardened coconut oil fatty acid glyceryl sulfates, alkyl sulfocarboxylic esters, alkyl sulfosuccinates, dialkyl sulfosuccinates, alkyl polyoxyethylene sulfosuccinates, and sodium (or ammonium or TEA) sulfosuccinic monooleylemides. Nonionic surfactants are, e.g., polyoxyalkylene alkyl ethers (or esters), polyoxyalkylene phenyl (or alkylphenyl) ethers, polyoxyalkylene naphthyl (or alkylphenyl) ethers, polyoxyalkylene etherse for surfactents ethers (or surfactents prepared by further adding a polyoxyalkylene to the phenyl group), polyoxyalkylene to the phenyl group), polyoxyalkylene hospies, polyoxyalkylene block polyoxyalkylene sorbitan fatty acid esters, polyoxyalkylene sorbital An aqueous solution according to the invention for the reductive deposition may contain, depending on its intended use, any of known reducing agents, surfectants, smoothening agents, semi-brighteners, brighteners, stabilizing auxiliary complexing agents, masking complexing agents, pH buffers, conductive salts and/or any of antioxidants or other additives. Among enionic surfectants are alkyl (or formalin condensate) - beta. Trapithal enseal fonce coid (or their salts), fatty acid condensate) - beta. Trapithal enseal fonce coid (or their salts), fatty acid soaps, alkyl sulfonates, alkylaiphenyl ether disulfonates, alkyl or alkoyly naphthalenesulfonates, alkyldiphenyl ether disulfonates, alkyl ether sulfonates, alkylaulfuric esters, polyoxyethylene alkyl phenol ether sulfuric esters, higher alcohol phosphoric monoesters, polyoxyalkylene alkyl ether phosphoric acids (phosphates), polyoxyalkylene alkyl phenyl ether phosphoric acids (phosphates), polyoxyalkylene alkyl phenyl ether phosphates, polyoxyalkylene consisting of copper, silver, gold, zinc, cadmium, indium, germanium, <u>tin.</u> lead, exsenic, antimony, bismuth, chromium, molybdenum, menganese, iron, cobalt, nickel, ruthenium, rhodium, palladium, omium, iriddium, and platinum. Where codeposition with such a merea lor metals is desired, the solution may further contain one or two or more compounds containing phosphorus, boron, or of metals contains one or two or more types of metals selected from the group As suitable surfactants, cationic surfactants include tetra-lower alkylammonium halides, alkyltrimethylammonium halides, hydroxyethyl alkyl imidazoline, polyoxyethylene alkyl methyl ammonium halides, alkylbenzalkonium halides, dialkyldimethyl ammonium halides, alkylamine hydrochlorides, alkylamine alkylamine hydrochlorides, alkylamine acetates, alkylamine olestes, The compounds that can be suitably used as <u>surfactants</u> are the cationic, anionic, nonionic, and amphoteric <u>surfactants</u> usually used in plating baths. They are used singly or as a mixture as desired. Ц Ц ш Brief Summary Text - BSTX (25): Brief Summary Text - BSTX (27): Brief Summary Text - BSTX (28): Brief Summary Text - BSTX (29): Brief Summary Text - BSTX (30): US 6436269 BI us 6322686 B1 US 6248228 B1 US 6183619 BI US 6183545 B1 10 % US 6251253 B1

US 6,183,545 B1 U.S. PATENT DOCUMENTS Caude et al.
Okutsi et al.
Chamand et al. References Cited (45) Date of Patent: (10) Patent No.: 63-259093 8-225985 8 Masakaza Yoshimoto, Shigeru Takatani Emiko Tanaka Masayuki Nishino: Yuji Kato, Yasuhino Kohashi Kyoko Kuba: Tesaya Kondo, Ketji Shomi; Ketgo Obata, ali of Ausati; Mitsuo Konatsu, Darati; Hldemi Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days. Inventors: Yoshiaki Okuhama; Takso Takeuchi; (54) AQUEOUS SOLUTIONS FOR OBTAINING METALS BY REDUCTIVE DEPOSITION Daiwa Fine Chemicals Co., Ltd. Nawafune, Takatsuki, all of (JP) United States Patent Hyogo-ken (JP) Okuhama et al. (73) Assignee: Notice: હ ε

Jun. 28, 1999 (21) Appl. No.: 09/340,894 Filed:

Foreign Application Priority Data 6 Jul. 14, 1998

C25C 372, C23C 18/36, C23C 18/34, C23C 3/20, C23C 3/24, C23C 3/26, C23C 3/36, C23C 3/38, C23C 3/46, C23C 3/36, C23C 3/54, C23C 3/56, C23D 3/10, C23D 3/20 C23C 18/31; C23C 18/32; C23C 18/38; C23C 18/42; (51) Int. CL.7

205/251; 205/253; 205/258; 205/259; 205/262; 205/263; 205/264; 205/265; 205/267; 205/269; 205/270; 205/271; 205/281; 205/290; 205/296; 106/1.25; 106/1.18; 106/1.19; 106/1.21; 106/1.22; 106/1.23; 106/1.25; 106/1.25; 106/1.25; 106/1.25; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1.29; 106/1. 205/239; 205/240; 205/241; 205/242; 205/243; 205/244; 205/244; 205/245; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205/246; 205 U.S. Cl. ... (23

205/299; 205/302; 205/311; 205/315 Field of Search 8

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(74) Airomey, Agent, or Firm-Akin, Gump, Strauss, Hauer & Feld, L.L.C. Primary Examiner-Helene Klemanski

ABSTRACT

10-198763

An aqueous solution for the reductive deposition of metals comprising, besides water,

(A) a phosphine of the general formula (1)



3

in which R., R., and R., denote lower alkyl groups, at least one of which being hydroxy-or amino-substituted lower alkyl group, and

(B) a soluble compound of a metal or a compound of a metal solublized through the formation of a soluble complex by said phosphine

12 Clahns, No Drawings

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TITLE:

J 介 주

Electroplating baths salts of aromatic hydroxy compounds and their use as brighteners

**4** 0

Brief Summary Text - BSTX (4):

or zinc alloys or tin alloys, onto metallic substrates, such as shaped metal articles or metallated plastic shaped articles, from aqueous acidic solution, a atticle an advantageous decorative appearance. Thus, in addition to the corresion-inhibiting effect or an effect which improves the mechanical properties of the shaped article, a decorative effect is often desirable. In order to obtain the desired effects, it is essential that the electroplating heaths contain certain assistants, since otherwise the metal coatings being deposited from addic solution are generally dull and frequently also irregular. A group of such assistants for acidic electroplating baths comprises, for example, conductive salts which are used for improving the conductivity of the baths. Another group of assists comprises the brighteners. In the electrodeposition of metals or alloys, in particular of zinc or tin bright coating is frequently desirable in order to give the electroplated

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Brief Summary Text - BSTX (177): Preferred metal salts are  $\overline{zinc}$  salts and  $\overline{tin}$  salts.

sulfate. If alloys of zinc, for are to be deposited onto with regard to the other components. They contain, for example,  $50-150 \ g/1$  of zinc chloride or the equivalent amount of zinc sulfate. If alloys of zinc, for example with cobalt and/or nickel and/or iron, are to be deposited onto metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/1 of cobalt sulfere and/or nickel sulfete and/or into sulfate or the equivalent amount of enother, water-soluble cobalt and/or nickel and/or iron salt. It is also possible to use the corresponding tin salts in equivalent amounts. Brief Summary Text - BSTX (181): The novel aqueous acidic electroplating baths have the usual compositions

Brief Summary Text \_\_BBTX (183):

A further conventional component of the novel aqueous acidic electroplating haths comprises; surfactants or wetting agents, in particular nonionic and ionic surfactants, which act as auxiliarly brighteners. Buitable nonionic aurfactants are disclosed, for example, in British Patent 1,149,106. These are adducts of ethylene oxide with fatty alcohols, for example with C.sub.8 -C.sub.18 -alcohols, or adducts of ethylene oxide with phenol or alkylphenols, in particular with nonylphenol. As a rule, 5-100 mol of ethylene oxide are subjected to an addition reaction per mole of alcohol or phenol.

Brief Summary Text - BSTX (184):
 Purther useful nomionic surfectants include poly(elkyleneimines).

5,951,841

another, water-soluble cobalt and/or nickel and/or ivon sait. It is also possible to use the corresponding tin salts in

chloride, which is usually present in a concentration of 100-202 gli in avoid ledenoishing bath. Other conductive salls are, for example, summontum chloride and socialm chloride, which are usually used in a concentration of equivation amounts.

A further conventional component of the battss comprises conductive salls, in purionlar sodium salls, polassium salls and ammonium sales. A smitable conductive salt is potassium.

example with Ce-C<sub>10</sub> slicotols, or adducts of ethylene oxide with phenol or allythenols, in particular with monyphenol and addition and for all one of a look are ampiced to a addition reaction per mole of alcohol or phenol. Polyoxyallylated maphthols may also be added.

Further useful notionic surfacents include poly A further conventional component of the novel aqueous cidic electroplating baths comprises surfactants or wetting tgents, in particular nonionic and ionic surfactants, which 1ct as auxiliary brighteners. Surable nomonic surfactants are disclosed, for example, in British Patent 1,149,106. These are adducts of ethylene oxide with fatty alcohols, for

ruttner useful notionic surfactants include poly (allyleneimines). Poly(allyleneimines) noty be used as such or they may be reacted with a cyclic extronant which consists of carbon, piydrogen and oxygen atoms. A description of the preparation of such compounds is disclosed in U.S. Pai. No. 2,824,857.

Suitable anionic surfactants are disclosed, for example, in U.S. Par. No. 3,787,296. These are mainly sulfated polyelethers, which are obtainable, for example, by an addition reaction of ephyleze oxide with farty alcobods, fany amines, amides of Co-Co-carboxylic acids and relaively long-chain first perde and a subsequem sulforation in each case. Sulfonness of polysultytens oxides or block copolymens of ethylene oxide and propylene oxide are also used as amonic surfactants

A further group of anionic surfactants is disclosed in EP-B-115 020. Sulforated and sulfatedally phenolethoxy of the general formula

(C,H,O),Y

where R is C.-C.m.-slkyl, X and Y are each a redical of the formula —SO<sub>2</sub>H or —SO<sub>2</sub>Me and Me is ammonium, an alkali metal or one equivalent of an alkaline earth metal or 50

In addition to such compounds, other suitable anionic surfactants are the suifonated and sulfared products whose polyether chain contains 1–25 propylene oxide or buylane oxide units. zinc atom and p is 5-50, are described.

DE-C-38 39 824 discloses anionic additives based on monobasic and polybasic ethersulfonic acids. These are prepared by individual or combined sulfopropylation and/or sulfobutylation of the following hydroxyl-containing com-

b) monohydric or polyhydric samrated or unsamrated aliphatic alcohols and monohydric or polyhydric, alkylared or nonalkylated phenols or naphthols, including their

The advantage of the sulfonated and sulfated alkylphenol alkoxylates is that they have an extremely high cloud point

so that the electrolytic deposition of the metal, in particular of zinc, can be carried out not only at 20-30° C. but also at 30-90° C., preferably 40-50° C.

Further suitable surfactants include phenol/formaldehyde s condensates and naphthalenesulfonic acid/formaldehyde

In addition to the stated surfactants, polyethylene glycols having molecular weights 200-1000 g/mol are also suitable auxiliary brighteners.

The surfactants and other auxiliary brighteners are used in the novel equevous seridic electroplating baths usually in amounts of 1–20, preferably 2–15, gft. It is also possible to use a mixture of a phirality of surfactants, or auxiliary brighteners. 5

The pH of the novel aqueous acidic electroplating baths is, as a rule, 2-7, preferably 4-5. It is established, for example, by adding acids, for example conventional mineral acids, such as sulfaric acid or hydrochloric acid.

The present invention furthermore relates to a process for the electroplating of shaped articles, which comprises 1. bringing a shaped article into contact with a novel actific electroplating bath and 2. carrying out electroplating. 2

By means of the novel process, for example, shaped in studied comprising metals, mithly comprising zon or steel, as me electroplated in order to protect them from corrosion and simultaneously to give them great brightness. The novel collection control of the propose give, with the entire, necknically televant current density range, very bright sand dwt-tile metal controls, for example, zon countings, they are quality of the coatings obtained to see east superior to the quality of the coatings obtained using beneryliteneacement. according to the prior art.

Synthesis Examples for compounds of the formula are I and II and Use Examples for novel acidic electroplating 3s baths are described below.

IV. EXAMPLES

The subjects of the present invention a illustrated by the following examples, in which further preferred individual feature of the invention are described.

Synthesis Examples

Synthesis Examples for some of the novel compounds of 45 the formulae I and II are described below.

Example 1

Preparation of the sodium salt of vanillidenescenne:

p) block polymers of ethylene oxide and/or glycidol with by g (0.032 mol) of vanilin were dissolved in 15 ml of propylene oxide and/or burylene oxide, and 8.3 ml of 50% strength sodium hydroxide b) monohydric or polyhydric saturated or unsaturated solution were added. There after, 10 ml of water were added b) monohydric or polyhydric saturated or unsaturated and stirring was carried out for 20 bours at room tempora-ture. The precipitated residue was weahed with acctours and cleed. 7 g (corresponding to a yield of 95%) of the title compound were obtained in the form of an orange-yellow solld The purity of the product was >97%. 2

5 AND METHOD FOR ELECTROPLATING BATH [58] Weld of Search 206725, 254; 106/1.05, 1.25, 1.29 C23D 3/56; C25D 3/60 zinc-tin alloy from pyophosphate electrolytes in the presence of surfaceans Zashch. Met. 22(4) 615-17 (Russ), 1986 (no month):English ab., article unavail. 205/244; 205/252; 205/253; Vagramyan et al. Some features of the electrodeposition of Inventors: Hitoshi Sakurai, Matsudo; Tadahiro Assignee: Dipsoi Chemicals Co., Ltd., Tokyo, Chruma, Funabashi, both of Japan **POREIGN PATENT DOCUMENTS** United States Patent U.S. PATENT DOCUMENTS OTHER PUBLICATIONS Igunathi et al. ..... Rekles References Cited 4,622,47 3/1967 Kobayash ... 4,701,244 10/1987 Nobel et al. Germeny Jan. 12, 1994 UNDING THE SAME Appl. No.: 180,345 8/1979 5/1983 12/1973 11982 11982 111984 Sakurai et al. Int Ci. US. CL 4,163,700 4,384,930 4,652,347 2185007 57-2795 57-2796 59-48874 Fled <u>Z</u> Ē Ē [2] 2 [36] USPAT USPAT USPAT USPAT USPAT USPAT A tinzinc alloy electroplating bath comprises an amphoteric <u>surfactant</u>, a water-soluble transous salt, a water-soluble <u>rinc</u> salt and a balance of water when the <u>tinzinc</u> alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case where the current density varies over a wide range. Therefore, the coating film waying the uniform alloy composition can be formed even on the substance having a complicated shape and the chromate treatment becomes satisfactory. As a result, the effect of the coating is improved, the resultent product is stable and the productivity is improved. Thus the <u>tin-zinc</u> alloy coating film having The present invention relates to a tin-zinc alloy electroplating bath and a method for electroplating using the same. In particular, the present invention relates to a tin-zinc alloy electroplating bath capable of stably forming a coating of a uniform alloy composition by keeping the plating alloy composition by keeping the plating alloy composition The tin-zinc alloy electroplating method attracted attention, and recently has come to be widely used as an industrial plating method for automobile parts and electronic parts, since the electroplated products have excellent corrosion resistance, aqueous salt solution resistance and solderability. A defect common to the conventional tin-zinc alloy PLANING BATHS is that the current density exerts a strong influence on the composition of the plating alloy. Namely, even when the current density during the plating is fixed, the current density distribution on the surface of the substance to be plated is not always even and, therefore, the composition of the plating alloy is Tin-zinc alloy electroplating bath and method for electroplating using the The plating baths heretofore proposed for the tin-zinc alloy electroplating include, for example, an alkaline cyanide bath, pyrophosphate bath, borefluoride bath, sulfonate bath, carboxylate bath and cyanide-free alkaline bath. Some of them are prectically used. Kind Codes  $\underline{\mathrm{Tin-zinc}}$  alloy electroplating bath and method for electroplating using the same a o ш □ D U US 5618402 A 5618402 a high quality can be provided. Brief Summary Text - BSTX (2): Brief Summary Text - BSTX (4): Brief Summary Text - BSTX (3): Brief Summery Text - BSTX (5): Document ID v Pages Abstract Text - ABTX (1): 13 6 DOCUMENT-IDENTIFIER: US 6248228 B1 US 6183619 BI US 6183545 B1 US 6179985 B1 US 5951841 A US 5902472 A US 5618402 A -- KWIC TITLE - TI (1): US-PAT-NO: TITLE: Same B 2000 CB 41 **○ ■ ■ × 4** 🕦 **1** Ø Ø 5 5 5 6 0 € 6 **9 € 6** ៤៦៨ 1 2 2 3

## [11] Patent Number: (45] Date of Patent: A

5,618,402

## (45) Date of Patent: Apr. 8, 1997 Surface Treatment Technology Abstract, vol. 29, No. 2, pp. 84, Mar./Apr. 1987, L. K. Bobrovskii, et al., "Electrodyte for Electrodeposition of Tin-Zinc Alloy Costings" (nat 1221)

Galvazorischmik, vol. 82, No. 9, p. 3046, Sep. 1991, "Galvanische Zinn-Zink-Uberzuge Als Cadmiumersetz" (ozt trans Dec. 2).

Prinary Examiner—Katuya L. Gargos Assisara Examiner—Edna Wong Attoracy. Agard. or Ferm—Oblon, Spivak, McClelland, Majer & Neusatt. P.C.

### ABSTRACT

A tin-zano alloy electroplating bath comparies an amphotonic surfactant, a water-soluble stammus sall, a water-soluble inte sall and a beliame of water. When the tin-zine alloy plating beth of the present invention is used, the formed coating film comprises a uniform alloy composition even in cass where the current density varies over a wide range. Therefore, the coating film having the miftorn alloy composition can be fourned overn on the substance having a compilicated stape and the chromate treatment becomes autifestory. As a result, the effect of the coating is improved, the resultant product is smalle and the productivity is improved. Thus the tin-zinc alloy coating film having a high quality can be provided.

16 Claims, No Drawings

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<b>Κ</b> <del>Τ</del>	US-PAT-NO: 5951841
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<b>(</b> ) 6	DIMX
) M	: 0
၃ ၜ	In the electrodeposition of metals or alloys, in particular of zinc or tin or zinc alloys or tin alloys, onto metallic substrates, such as shaped metal
ď	atticles or metallated plastic shaped articles, from aqueous scidic solution, a bright coating is frequently desirable in order to give the electroplated
0	article an advantageous decorative appearance. Thus, in addition to the corrosion-inhibiting effect or an effect which improves the machanical
<b>a</b>	properties of the shaped article, a decorative effect is often desirable. In order to obtain the desired effects, it is essential that the electronic in
4	nce otherwise the
1 c	irregular. A group of such assistants for acidic electroplating baths comprises for evenule conductions.
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۵	Reissue 27 999)
<b>(4)</b> (4)	compounds. Arcmatic carboxylic acids and arcmatic aldehydes and ketones are mentioned as the latter. Explicitly mentioned are, inter alia, cinnamic acid, cinnamaldehyde, benzolc acid, benzal are and attentions.
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96	sulfam aldeh
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49	Brief Summary Text - BSTX (177): Preferred metal salts are zinc salts and tin salts.
<b>A</b>	Brief Simmery West - Domy /101/
6	baths have the usual compositions
æ	oride or the equivalent amount of z
<u> </u>	metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/l of cobalt sulfate and/or nickel milfate and or nickel
	amount of another, water-soluble cobalt and/or nickel and/or iron salt. It is
- Acceptant	

Ö	nited St	United States Patent [19]	Ξ	Patent Number: 5,951,841
¥.	Wehlage et al.		[45]	Date of Patent: Sep. 14, 1999
[54]		ELECTROPLATING BATHS SALI'S OF AROMATIC HYDROXY COMPOUNDS AND THEIR USE AS BRIGHTENERS	4,226,682 4,229,268 4,242,183	10/1980 10/1980 12/1980
[75]	Inventors:	Inventors: Thomas Wethage, Speyer, Ulrich Schröder, Frankential, Affred Offring, Bad Dürkheim, all of Germany	5,422,500 5,422,500 PC	6/1995
[73]	Assignee:	BASF Aktlengesellschaft, Ludeigshafen, Germany	28 48 261 41 19 341	221 7/1980 Germany. 341 12/1982 Germany. OTHER PARTICATIONS
园		08/860,301	Genshum	d Hideo Nakao.
[86]	PCT Filed: PCT No.:	Dec. 22, 1995 PCT/EP95/05090	ring 2-bromo-	ting compounds, XIII. Reaction of 2-bronno-Tinethoxytropune with active methylene compounds, Term Physic Bull Technol 1947, 2000.
	§ 371 Date:		(1965). Al	(1965). Abstract taken from Chemical Abstracts 63:4274g.
[87]		FCT Pub. No.: WO96/20152	Synthetic	Kofchi Araki, Hironobu Hashimoto, and Juji Yoshimura.  Synthetic Studies on Glycocinnamoyspermidines. Synthe-
	PCT Pub. Dat	PCT Pub. Date: Jul. 4, 1996	bohydr. R.	bohydr. Res., 109, 143-60 (English). Abstract taken from
[30]	Foreign,	Foreign Application Priority Data	Chemical Patent Abs	Chemical Abstracts 98:54363, 1982. Patent Abstracts of Japan, vol. 14, No. 43 (C-0681), Nov.
Dec	Dec. 23, 1994 [DE]	Oermany 44 46 329	6, 1989, 3	6, 1989, Jp 1-275-552, Apr. 28 1988.
[52]	Int. Cl.* U.S. Cl. 205/314	Int. CL	Primary E Assistant I Attorney, Maier & N	Primary Examiner—Kaitaryn Gongos Asststant Examiner—Wealey A. Nicolas Aftorney, Agent, or Firm—Oblon, Spivak, McClelland, Maier & Neissdaft, P.C.
[58]	Field of Search 205/303, 106/1.05; 549/2	307, 308, 311, 312, 3 87, 558/401, 568/308,	[57] Salts of arr	[57] ABSTRACT Sals of aromatic hydroxy compounds are used as brighten- ers in actific electroplating baths. Purthermore, acidic elec-
[96]	1 S 11	References Cited	layers oute	uppaints battls for the electrolytic deposition of metallic is layers onto shaped articles comprise, as brighteners, at least one novel sait of an aromatic hydroxy compound. Finally,
3 6		4/1974 Korpinactel	shaped arti	shaped articles are electroplated by a process using the nove! acidic electroplating baths.
คั	3,891,520 6,1975	5 Todt et al		17 Claims, No Drawings

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Other additives Amount plated product 0.2 A/dm.sup.2 5 A/dm. sup.2 A/dm.sup.2

None -- Dull 31.2 40.3 43.0 2 Aromatic aldehyde 0.1 g/l Semiglossy 28.0
38.6 39.2 3 None -- Dull 25.5 38.8 41.2 4 None -- Dull 20.7 35.6 34.7 5
DIPSOL. RTM. De-FR-7 01 g/l Semiglossy 20.1 35.135.7 6 None -- Dull 21.3
38.4 39.4 7 DIPSOL. RTM. 32-2408 8 m/l/l Semiglossy 20.5 35.1 38.5 8 None
-- Dull 27.0 37.6 41.0 9 None -- Dull 21.5 34.9 37.7 10 DIPSOL. RTM. 32-2408
8 m/l/l Semiglossy 12.3 34.4 38.2 11 Polyoxyethylene 5 g/l Semiglossy 20.5
35.6 39.3 laurylamine (15 mol ethylene oxide adduct) 12 None -- Dull 23.3
36.6 39.0 13 None -- Semiglossy 25.0 38.9 40.5 14 Aliphatic amine/ 2 mill semiglossy 25.0 38.9 40.5 14 Aliphatic amine/ 2 mill product 15 None -- Dull 54.6 68.6 74.6 16 Epoxy compound/ 2 g/l Semiglossy 25.9 5 37.5 32 DIPSOL RTM. SZ-2408 8 m/l Semiglossy 12 35.37.5 32 DIPSOL RTM. SZ-2408 8 m/l Semiglossy 12 35.37.5 32 DIPSOL RTM. SZ-2408 8 m/l Semiglossy 9.0 (15 mol ethylene oxide adduct) 35 None -- Sponsy surface -- -- 36 Aliphatic aminodict and ester/ nhthalic minudictal minudictic aminodict and ester/ nhthalic minudictal minudictal amiglossy 8.4 15.0 19.7 organic acid ester/ reaction product 37 Polyethylene glycol 5 g/l Semiglossy 18.1 40.2 51.9

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Claims Text - CLTX (8):

A tin-zinc alloy electroplating bath which comprises:

Claims Text - CLTX (1):

The tin-zing alloy electroplating bath of claim 1 wherein the amphoteric surfactant is an imidazoline.

Claims Text - CLTX (9):

2**3**20232**3**4•

 The tin-zinc alloy electroplating bath of claim 1 wherein the emphoteric surfactant is present in an amount of 0.3 to 15 g/l. Claims Text - CLTX (10);

4. The tin-zinc alloy electroplating bath of claim 1 wherein the water-soluble stannous salt is present in an amount of 5 to 50 g/l in terms of metallic tin.

5. The tin-zinc alloy electroplating bath of claim 1 wherein the water soluble  $\overline{zinc}$  salt is present in an amount of 25 to 40 g/l in terms of Claims Text - CLTX (11); metallic zinc.

Claims Text - CLTX (12):

wherein R7 represents an alkyl group having 8 to 20 carbon

5,618,402

The amphotenic surfactants of glycine type are proferably those having a structure of the following formula (5) or (6):

(R\*-NHCH,CH,), NCH,COOH R"-NHCH, CH, NHCH, COOH

6

wherein Re represents an alkyl group having 8 to 20 carbon

The amphotence surfactants of amide type are preferably those having a structure of the following formula (7):

R"—CONHCH, CH, NHCH, COOL

wherein R<sup>o</sup> represents an alkyl group having 8 to 20 carbon

Those amphoteric surfactants can be used either singly or in combination of two or more of them.
The tin-zinc alloy electroplating bat

amount of usually 1 to 100 gf. (in terms of menalite this), preferably 5 to 50 gf. and a water soluble size salt such as zine saltiets in an emount of usually 10.2 to 80 gf. (in terms of metallic size), preferably 25 to 40 gf. Perticularly preferably 3 to 40 gf. Perticularly preferably 3 to 7 earther amounts of metallic size, preferably 3 to 7 earther amounts and a carboxylic acid having 1 to 15 carbon atoms, preferably 3 to 7 carbon stoms and a string acid or glucomic acid, 3 to 300 gf of pyrophospharic acid or 20 to 400 gf. An outliness brightness or acid, the can be added to the 35 star contract. The tin-einc alloy electroplating barhs of the present 30 invention include, for example, an alkaline cyamide bath, pyrophosphate bath, burofluoride bath, allicofluoride bath, water soluble stannous sait such as stannous sulfate in an sulfonate bath, carbonylate bath, cyanide-free alkaline bath, gluconate bath and organic acid bath. The bath contains a

plaing bath. For example, 0.1 to 20 gd of a water-soluble brightener obtained by reacting pathalic unhydride with a reaction product of an alighestic amine and an organic acid cuter can be added to the bath.

When the plasting bath of the present invention is used, an of intended the above alloy coasting having a thickness of, for example, 0.5 jun to 0.5 mm can be formed by the electropating on a menta such as from, raided, copper or an alloy of them. Further, by varying the ratio of the lo zrior in the plating bath, writous the ratio and the normal plating as an obtained. For example, a composition having a zric content of 5 to 3% by welght is used for the electric counter of 5 to 3% by welght is used for the electric counter of 15 to 45%. solution and to correston is necessitated; and a composition having a sinc content of 45 to 90% by weight is used for the by weight is used when a high resistance to an aqueous sait formation of a coating baying a high corrosion resistance which is to be exposed to air.

limited, the plating bath temperature is preferably 10° to 70° C, more preferably 10° to 40° C, and the current density is urplating is not limited, but preferably I minutes to 2 hours, more preferably 5 minutes to I hour. In this connection, the substrate is a cathode and tin-time alloy is an anode. A Although the efectroplating conditions are not particularly preferably 0.1 to 10 A/dm2. The time period for the eiec-

weight ratio of the no zinc in the amode is optional but preferably the ratio may be the same as in the alloy combiny position formed on the substrate.

(6): The contrib formed to tusing the electroplating bath of the present invention can be transferd with a chromate by an conducted by, for example, a method described in 1. P. KOKOKU No. Sho S#1100.

(9) KOKOKU No. Sho S#1100.

(10) When the fire-zine alloy plating bath of the present invention is the formed contribution.

into composition even in case the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the uniform alloy composition can be formed even on the substrate having a compliment chape, and the chromate is treatment becomes statisfactory. As a result, the effect of the born to the productivity is improved. The substraint product is stable and the productivity is improved. Thus the increase all the productivity is improved. Thus the increase and film having a king quality can be provided.

The following Examples will further lithurent the present investigation. The composition of the plainty bath and the plaints conditions can be changed depending on the object.

The basic tin-zine alloy plating bath used in the Examples 25 of the present invention are given in Table 1.

EXAMPLE 1

TABLE 1

Samples	Pyrophos bath	Surnous pyro- phosphau. (ID gl.) Zue pyrophosphau (40 gl.) Pyrophosphaus	Putarsium bydroxide for bulk 25° C.
Besic plants but thed to Examples	Observer back	Stemeous solino (40 g/l) Zine sultime (40 g/l) (130 g/l)	Association with the Cook graph of Cook grap
<b>W</b>	Charte beth	Bath composition Stamous suffice (40 g/l) Zire suffice (40 g/l) (40 g/l) (40 g/l) (100 g/l)	Ammunium sulface (80 g/l) pH adjustor Sodforn hydroxida or animonia weire Plening beth textp

wherein an iron steet was used as the cathode and a tin-zinc alloy sheet (weight ratio of the to zinc is 90/30) was used as above-mentioned bath temperature for 10 to 60 min, In this Example, the electroplating was conducted at the the anode and the current density was 0.2 to 5 A/dm2

The compositions of the tin-zinc alloy plating bath con-taining the amphoteric surfactant used in the Kample and also of the coating alloy film obtained from the bath are given in Table 2,

For comparism, the compostitons of the amphoteric surfactant-free pisting bath and also of the coating alloy film obtained from the bath are also given in Table 2.

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An electroplating bath for depositing tin or a tin alloy with satisfactory brightness, which comprises a mother bath of a pH-value ranging from 4 to 8 and containing citric acid or its salt, an ammonium salt and a water-soluble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener,

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Brief Summary Text - BSTX (6):

In the printed specification for said USSR Inventor's Certificate, there is
a disclosure that dextrine and gelatine are added as brighteners to attain a
finer and crystalline tim-zinc alloy deposition with a brightness. However,
the "brightness" to be attained by this Inventor's Certificate process is of
the degree "dull" or "mat" among the brightness degrees comprising bright (mirror bright), semi-bright, dull, mat and dendrite.

Brief Summary Text - BSTX (7):

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an organic acid ester and then further reacting the reaction product with phthalic eaid enhydride, or adding to the final reaction product with eldebyde as a co-brightener (Jap. Pat. Appl., No. 148 687/1974 which was early opened under the number of 75 632/1976). The brightener is advantageous in attaning a "bright" or "semi-bright" tin-sinc alloy electroplating regardless of a kind of the metal to be pitched or an electroplating both to be employed. The brightener, however, has a practical disadvantage that the range of working current density required during the electroplating is relatively In order to improve the brightness, one of the present inventors has proposed together with others a brightener for time alloyal ectroplatings, which is a water-soluble polymer obtained by rescring an aliphatic amine with

Brief Summary Text ~ BSTX (13):

In addition to the water soluble polymer, at least one aldehyde compound may be added as a co-brightener. As the aldehyde compounds, formaldehyde, acted deviated by the propional dehyde, glycoth, succindialdehyde, formaldehyde, or the like alphatic one and benzaldehyde, prolublehyde, saproaldehyde, proproaldehyde, proproaldehyde, protolublehyde, salcylaldehyde, be employed solely or as a mixture thereof. These aldehyde compounds the saployed solely or as a mixture thereof. These aldehyde compounds the propression of a mixture thereof the brightner when using either solely or classified as "bright" or "mirror bright" to the tim or timalloy polymer as main brightner. In this connection, please note that if no pelymer as main brightnerer. In this connection, please note that if no be deposited on a base material assumes a brightness classified as "semi-bright" or "dull".

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Brief Summary Text - BSTX (20):

The aldehyde compound as co-brightener is added to the mother bath in an amount of  $0.1\ \text{to}\ 0.5\ \text{g}/1$ . The excessive addition does not give any bad influence but is meaningless.

Detailed Description Paragraph Table - DETL (1):

Composition of mother bath: Sn80. sub. 4 S0 g/l Ammonium citrate  $100~{
m g}/1$ 

E United States Patent garashi et al.

4,168,223 Sep. 18, 1979

> [54] ELECTROPLATING BATH FOR DEPOSITING TIN OR TIN ALLOY WITH BRIGHTNESS

U.S. PATENT DOCUMENTS

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3

Consoby et al.

10/1971 10/1973

Shuji Igarashi, Yoshikaza Pujisawa; Toshio Igarashi, ali of Tokyo, Japan Inventors: 5

Dippol Chamicals Co., Ltd., Tokyo, Assignee Ē

[21] Appl. No.: 960,944

Nov. 15, 1978 Filed: 22

52-136731 Foreign Application Priority Data Nov. 16, 1977 [JP] Nov. 16, 1977 [JP] 

204/44, 120, 123; 106/1.25, 1.22 CISD 3/32; CZSD 3/60 -- 204/43 S; 204/44 [38] Field of Search US CL Ę

· FOREIGN PATENT DOCUMENTS Potil Doti et al 1469547 4/1977 United Kingdom .. 3,892,637 7/1975

Phway Examiner—G. L. Kaplan Morney, Agent, or Firm—Birch, Stewar, Kolasch, and 204/435 报

An electroplating bath for depositing in or a tin alloy with satisfactory brightness, which comprises a mother bith of a pH-vulte ranging from 4 to 8 and constaining citrio acid or its salt, an amonotium salt and a water-acid. uble polymer as a brightener. The bath may further comprise an aldehyde compound as a co-brightener, ABSTRACT 5

S Claims, No Drawings

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	230) ((205/244) or (205/245) or (205/246)).CCLS. 266) (1(205/252) or (205/253) or (205/254)).CCLS. 468) 11 or 12 121) 13 and 15 146362) surfactant or surfactants 17669) surfact adj active adj (agent or agents) 174186) 17 or 18 17572) and and 110 17572) and adhyde or aldehydes 1760482) ketone or ketones 1760482) ketone or ketones 1771) 114 or 115 178161 hetorocyclic near2 carboxylic 17810 hetorocyclic near2 carboxylic 17811 117 or 118 18) 16 and 119 18) 16 and 119 19) 16 and 119		ID Issue Date Pages Title	11	20020425 5	20030121	20020820 8	19990914 13	19930423	19930423	A 19830524 10 Electroplating baths, additives therefor an			splong   @ Chemps   B. Way no.   B. New cas.   El 1001870.
	ь <u>в ввесена</u>	₩ nDc	U 1 PT P	ц			С   С   С	1302000 D D D D		2402026		# res Opens Tring	Ready	Start   S & S II *     S Hibos : M.   II E

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United States Patent	- 1	[54] ELECTROPLATING BATHS SALITS OF AROMATIC HYDROXY COMPOUNDS AND THEIR USE AS BRIGHTENERS [75] Inventors: Thomas Wehlege, Speyer, Ulrich Schwöder, Frankenini, Alfred Oftring, Bad Dürkbein, all of Germany	[73] Assignee: BASF Aktiengeerijechaft, Ludvigahafen, Germany	[21] Appl. No.: 08/960,301 [22] PCT Filed: Dec. 22, 1995 [86] PCT No.: PCT/EP95/05090 § 371 Daus: Oct. 6, 1997	\$ 102(c) Dute: Oct. 6, 1997 [87] PCT Pub. No.: WO96,20152 PCT Pub. Date: Jul. 4, 1996 [30] Forelow Amilication Debote: Date	Field of Search 205;303, 307, 308, 311, 312, 3106;105; 559;401; 560;51; 205;30; 305;314; 549;287; 558;401; 569;51; 205;30; 307, 308, 311, 312, 3106;105; 549;287; 558;401; 568;308;	564/123 [56] Reftrences Cited U.S. PATENT DOCUMENTS Re. 27,999 4/1974 Korpin at al. 3,462,459 6/1975 Tolt et al. 2,591,520 6/1975 Tolt et al. 255/314			in the bath in the
Document 1D v Rages 1   3   1   1   5   C   P   Kind Codes   US 6508927 B2   11   C   C   C   C   C   C   C   C		4       Us 54095685 A       7       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0       0	X	DOCUMENT-IDENTIFIER: US 5951841 A  ***See image for Certificate of Correction**  TIFLE:  Blectroplating baths salts of aromatic hydroxy compounds  and their use as brighteners	Brief Summary Text - B9TX (4): In the electrodeposition of metals or allows in section.	or zinc all articles or bright coetra article and corrosion-in properties order to ob beths contaided intreculer.	A group to such assistants for actdic electroplating baths for example, conductive salts which are used for improving the y of the baths. Another group of assists comprises the brighteners.  If you say the baths and the same say of electroplating which contain amonyments and the sate of say and the same say and the say of the latter. Explicitly mentioned are, inter alia, cinnamic acid, benzalacetone and ethyl benzoylacetate.	Brief Summary Text - BSTX (177): Preferred metal salts are $\overline{ ext{zinc}}$ salts and $\overline{ ext{tin}}$ salts.	Brief Summary Text - BSTX (181):  The novel aqueous acidic electroplating baths have the usual compositions are novel aqueous acidic electroplating baths have the usual compositions with regard to the other components. They contain, for example, 50-150 g/l of a comple with cobalt and/or nickel and/or iron, are to be deposited onto metallic shaped articles, the baths additionally contain, as a rule, 1-30 g/l of cobalt sulfate and/or nickel sulfate and/or iron sulfate or the equivalent anount of another, water-soluble cobalt and/or nickel and/or iron sulfate and/or iron salt. It is	Claims Text - CLTX (144):  9. An acidic electroplating bath as claimed in claim 1, wherein the bath comprises at least one metal salt selected from the group consisting of zinc salts and tin salts.  Salts and tin salts.  Salts and Electroplating & Champs   @ Code po.   @ Number   @ Num

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4 7	Brief		Summary Text	B												•••••
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(di	tin,	for	example	that the nickel, c	the electrolyte , cobalt, copp		lyte co		contains r and/or		other	other heavy metal	heavy metal	met	cal salts besides	
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the state of the workplace or its positioning sad dise. DE-A-26 09 146 describes a process for coloring in the electrolytes, in which throwing power is established trical and geometric parameters, such as for examp

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through the particular circuit and voltage strangement. 5 DEA-A-2 & 655 describes the use of a combination of th(II) salts and since all and voltage strangement. 5 DEA-A-2 & 665 describes the use of a combination of th(III) salts and since all and also arounaire carboxylic and sultain acid and also arounaire carboxylic and sultain acid and both ed carboxylic and sultain acid and solved as and carboxylic and sultain the electrolytic coloring of sandically oxidized sulminum in general argument in an acid to be obtained in particular when the pH value is between 1 and 1.5, pH sultisument to 1.1.3 is a basic percequite for good electrolytic coloring. For the standard of whether the organic soles added have an effect on throwing power, nor is the throwing power and mand of whether the coganic soles added have an effect on throwing power, nor is the throwing power and throwing power which good throwing power is guaranteed to by the use of special gomesty in the coloring that, in standard, and a destrin and/or thiours and/or again sultained, and a destrin and/or thiours and/or again and white good throwing process in electrolytic power be surranteed to by the use of special gomesty in the coloring that it is stall to guarantee uniform coloring. The disselvantee of throwing power because the desposition process in electrolytic power because the adopticing process in electrolytic coloring differs significantly from that in electrolytic coloring differs significantly from that in electrolytic powers to an electrolytic coloring differs a significantly from that in electrolytic processive measurement in presenting an electrolytic or consistent the consistent in the document in presenting an electrolytic or consists. question to possible methods of measuring the improve-

ments in throwing power.

In addition, Buropean patent application EP-A-354
365 dearnine a process for the electrolytic coloring of
anotized aluminum furfaces using metal salts, in which
the artitoridents corresponding to general formules I
and IV (cf. the claims) are used together with the throwing power improvers p-tolerne sufrain acid and-for nephthalene sufraio acid. However, the throwing power improves mentioned in this document lead du-ing electrolysis to foul-emelling decomposition prod-ucts so that these throwing power improvers are no

## DESCRIPTION OF THE INVENTION

Object of the Invention

Now, the problem addressed by the present invention was to provide a new electrolyte additive for a sulfurio 50. acid coloring bath containing int(I) for the alternating current coloring of anodized aluminum surfaces which would overcomes the problems known from the prior art discussed in the foregoing, such as guaranteeing listing subtility of the coloring bath, svicking the oxide, then of Sn(II) and, at the same time, guaranteeing good throwing power.

### SUMMARY OF THE INVENTION

emionidant and at least one throwing power improver, 65 characterised in that the electrolyte additive contains a) as emionidant at least one compound corresponding to general formulae I to IV: Accordingly, the present invention relates to as electrolyte additive for a sulfune acid coloring but on-taining tm(II) for the alternating-current coloring of anodized aluminum surfaces containing at least one

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in which
R1 and R2 represent bydrogen, alkyl, aryl, alkylaryl, alkylaryl sufform exid, alkyl suffonio acid
containing 1 to 22 carbon atoms and alkali metal
asks thereof and

R? represents one or more hydrogen and/or alkyl, arryl alkylaryl molecties containing 1 to 22 carbon strons, at least one of the substitutus R!, R! and R not being hydrogen, and D as throwing power improver at least one aromatic outboxylic and corresponding to general formula. V.

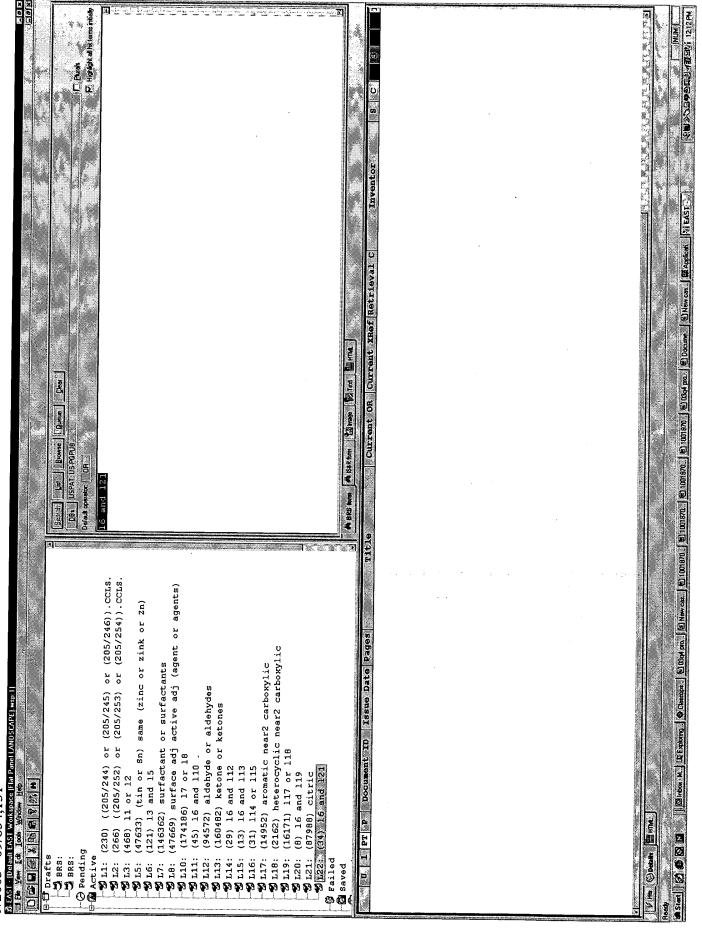
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inich in which

R! to R! represent hydrogen, hydroxyl, carboxyl
and/or suifonio acid groups.

The present invention also refarse to a process for the
alternative-current coloring of anotized sluminum surfaces in a suifunic sci coloring bath constitute the characterized in them electrolyte additive as defined
slow- seed for electrolyte coloring in the suifunic
calc coloring bett containing the fluid as a serior coloring in the suifunic
calc coloring seth containing the fluid as a few parts of 10 to 30 ° C. and with an
alternative current voltage with a frequency of 50 to 60
here and a terminal voltage of 10 to 23 V,
or might suitar advantage of the electrolyte additive socontain to the invention He in the me of ordistion-suitable, water-scieble strowing power improvers. It is parficularly after relativaly long periods of operation that

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A tin-based, two-component alloy electroplating composition comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a zinc, cobalt, hismuth and copper salt, 20 to 200 g/l of methanesulfonic acid, 10 to 300 g/l of a complexing agent provides a plating layer having excellent corresion resistance and solderability to electronic devices such as lead frames, Brief Summary Text - BSTX (17):

The conductive compound used in the inventive plating composition not only further enhances the conductivity of metal ions but also increases the stability of the plating composition to provide uniform plating and an improved current efficiency. The conductive compound may include various acids and current efficiency. In accordance with one aspect of the present invention, there is provided a tin alloy electroplating composition comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a line, cobblt, bismuth and copper salt, 20 to 200 g/l of methanseulfonic acid, 10 to 300 g/l of a conductive compound, and 0.5 to 50 g/l of a completing agent. salts thereof. Preferable conductive compounds are <u>citric</u> soid, sulfuric soid, amonium sulfete, amonium citrate, sodium acetate, sodium carbonate, sodium gluconate or potassium pyrophosphate. One or more conductive compounds may be employed in an amount ranging from 10 to 300 g/l in the inventive composition. Brief Summary Text - BSTX (13):

The novel <u>tin</u> alloy plating composition of the present invention comprises:
two metallic components, i.e., tin and a second metal selected from the group
consisting of <u>minc</u>, cobalt, biswuth and copper; methanesulfonic acid; a
conductive compound and a complexing agent. As a source of tin, various tin
compounds such as stannous methanesulfonate, stannous sulfate, stannous
chloride and sodium stannate are employed in an amount ranging from 20 to 500 1 L of a tin-zinc alloy plating composition was prepared by dissolving the following ingredients in distilled water. ser · L22: (34) 6 and 21 I US 6176996 B1 | Tag. S I Doc. 6/34 |SOBTED | I Format : KWI Tin alloy plating compositions connectors and printed circuit boards. Detailed Description Text - DETX (13): US 6176996 BL Brief Summary Text - BSTX (11): - ABTX (1): ្ដា g/l in the composition. DOCUMENT-IDENTIFIER: us 6183545 B1 us 6582582 B2 US 6508927 B2 US 6500886 B1 US 6436269 B1 US 6176996 B1 US 5618402 A US-PAT-NO: Abstract TITLE: ◎壓圈 ※ ₹ **4** 9] ත වරර තත 眘

United States Patent

US 6,176,996 B1 Jan. 23, 2001 (45) Date of Patent: 10) Patent No.:

205/253 205/25

5,769,381 . 6/1998 Sakurai et al. ..... 5,674,374 \* 10/1997 Salaurai et al.

(54) TIN ALLOY PLATING COMPOSITIONS

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Hakjang-dong, Sasang-gu, Pusan (KR), 617-020 Sungsoo Moon, #265-12, Inventor: 99 €

(74) Attorney, Agent, or Firm-Anderson Kill & Olick, PC Primary Examiner-Kishor Mayekar

Under 35 U.S.C. 154(b), the term of this patent shall be extended for 0 days. Notice:

ABSTRACT

Appl. No.: 09/181,395

Oct. 28, 1998

Filed:

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tion comprising 20 to 500 g/l of a tin salt, 1 to 100 g/l of a metal salt selected from the group consisting of a zinc, cobalt, bismuth and copper salt, 20 to 200 g/l of methane-A tin-based, two-component alloy electroplating composi-97-56368 C25D 3/56

sulforic acid, 10 to 300 g/1 of a conductive compound, and 0.5 to 50 g/l of a complexing agent provides a plating layer having excellent corrosion resistance and solderability to electronic devices such as lead frames, connectors and

Foreign Application Priority Data Field of Search Oct. 30, 1997 (KR) (51) Int. Cl.<sup>7</sup>. (52) U.S. Cl. ... (58) Field of S 8

. 205/254–252; 106/1.25 U.S. PATENT DOCUMENTS References Cited

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205/254

5,296,128 \* 3/1994 Gernon et al.

printed circuit boards.

7 Claims, No Drawings

ASIENT | ON BOOK | Michael - Michae

A lead frame was plated with 1 L of the resulting tin-zinc alloy plating composition at an electric current of 10 A/dm.sup.2 to give an alloy plating

Detailed Description Text - DETX (14);

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alloy electroplating bath is not particularly limited in the present invent it is preferably 0.01 to 30 g/l, more preferably 0.3 to 15 g/l. When it is below 0.01 g/l, the effect is insufficient and, on the contrary, when it exceeds 30 g/l, the bath is foamed during the plating and the current efficiency is lowered

Detailed Description Text - DETX (12):

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The tirring alloy electroplating beths of the present invention include, for example, an alkaline cyanide bath, pyrophosphate bath, borofluoride bath, salicofluoride bath, sulforete bath, sulforete bath, sulforete bath, sulforete bath, sulforete bath, supplied free alkaline bath, gluconate bath and organic acid bath. The bath contains a water soluble stannous salt such as stannous sulfate in an amount of usually 1 to 100 g/l (in terms of metallic th), preferably 5 to 50 g/l, and a water soluble zing salt such as zing sulfate in an amount of usually 0.2 to 80 g/l (in terms of metallic zing), preferably 25 to 80 g/l, and a water soluble zing salt metallic zing), preferably 25 to 80 g/l of a carboxylic soid having 1 to 15 carbon atoms, preferably 3 to 7 carbon atoms such as citric acid or gluconic acid, 30 to 300 g/l of pyrophosphoric acid or 20 to 400 g/l of sulfamic acid. The pH of the bath ranges from 3 to 10.

Detailed Description Text - DETX (14):

When the plating bath of the present invention is used, an intended tin-zinc alloy coating having a thickness of, for example, 0.5 mu mo to 0.5 mu and be formed by the electroplating on a metal such as iron, nickel, copper or an alloy of them. Further, by varying the ratio of tin to zinc in the plating bath, various tin-zinc alloy coating compositions can be obtained. For example, a composition having a zinc content of 5 to 5% by weight is used for the electric contact or the like, a composition having a zinc content of 15 to 45% by weight is used for occrosion is necessiteted; and a composition having a zinc content of 15 to by weight is used for the formation of a coating having a zinc content of 45 to 90% by weight is used for the formation of a coating having a high corrosion resistance which is to be exposed to air.

Detailed Description Text - DETX (15):
Although the electroplating conditions are not particularly limited, the plating bath temperature is preferably 10. degree. to 70. degree. C. 70. more preferably 10. degree. to 40. degree. C. and the current density is preferably 0.1 to 10 A/dm.sup.2. The time period for the electroplating is not limited, but preferably I minutes to 2 hours, more preferably 5 minutes to 1 hour. In this connection, the substrate is a cathode and <u>timerine</u> alloy is an anode. A weight ratio of tim to zinc in the anode is optional but preferably the ratio may be the same as in the alloy composition formed on the substrate.

Detailed Description Text - DETX (17):

When the timezine alloy plating bath of the present invention is used, the formed coating film comprises a uniform alloy composition even in case the current density varies over a wide range. Therefore, the coating film having the uniform alloy composition can be formed even on the substrate having a complicated shape, and the chromate treatment becomes satisfactory. As a result, the effect of the coating film is improved, the resultant product is stable and the productivity is improved. Thus the timezing alloy coating film having a high quality can be provided. **₹**ŋ௧ ₽₡₡₵₵₵₵₳₡₵₽₹₽₡₢₦₠₳₢₠₢₲₳**○**■₽₳

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TIN-ZINC ALLOY ELECTROPLATING BATH AND METHOD FOR ELECTROPLATING

<u>7</u>

USING THE SAME

Inventors: Hitoshi Sakurai, Matsudo; Tadahiro Assignee: Dipsol Chemicals Co., Ltd., Tokyo, Ohmuma, Funabashi, both of Japan

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## **45**

### Patent Number:

5,618,402 Surface Treatment Technology Abstracts, vol. 29, No. 2, pp. Apr. 8, 1997 Date of Patent:

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Attorney, Agent, or Firm-Oblon, Spivak, McClelland, Primary Examiner-Kathrya L. Gargos Assistant Examiner-Edna Wong Maicr & Neustadt, P.C.

C23D 3/56; C25D 3/60

Jan. 12, 1994

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Appl. No.: 180,345

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205/244; 205/252; 205/253;

206/253, 254; 106/1.05, 1.25, 1.29

[58] Field of Search US. CL EL CL. ij E

[51] [52]

U.S. PATENT DOCUMENTS

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coating film comprises a uniform alloy composition even in position can be formed even on the substance having a improved. Thus the tin-zinc alloy coating film having a high A tin-zinc alloy electroplating bath comprises an amphoteric surfactant, a water-soluble stamous salt, a water-soluble zinc salt and a balance of water. When the un-zinc alloy pizting bath of the present invention is used, the formed case where the current density varies over a wide range. Therefore, the costing film having the uniform alloy comcomplicated shape and the chromate treatment becomes the resultant product is stable and the productivity is satisfactory. As a result, the effect of the coating is improved. quality can be provided.

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Summery Text - BSTX (46):

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derivatives may be added. Atomatic carbonyl compounds such as benzylidene acetone, chlorobenzaldehyde, cinnamic acid, benzoic acid, or nicotinic acid may also be used to enhance leveling and brightness. Additionally, to further enhance brightness, sulfornimides and sulfornimides can be employed in chloride and/or sulfate containing baths of the types described in copending U.S. patent application Ser. No. 850,465, filed Apr. 15, 1986, the teachings of which are incorporated herein by reference. Zinc alloy baths may also contain potassium chloride, sammonium sulfate, ammonium chloride, sodium and/or and the like, to improve the conductivity of the bath. Additional supportive additives such as aluminam sulfate, polyscrylamides, thioureas, or the like may also be added to the bath to improve the crystal structure of the zinc alloy Zinc alloy baths may also contain various other additives or agents. In some cases a perticular additive or agent may be useful for more than one purpose. Examples of additional ingredients which may be employed in the zinc alloy baths include buffers and hath modifiers such as boric acid, acetic acid, ammonium sulfate, sodium acetete, ammonium chloride and the like. For chloride containing baths, carriers such as polyalkoxylated ethers such as alcohols, phenols, napthols or acetylenic glycols and their anionic and cationic solution. The preferred chelating agents are citric acid, gluconic acid, glucoheptanoic acid, tartaric acid as well as their alkali metal, ammonium, zinc, cobalt, or nickel salts. Also triethanolamine may be used. The quantities used should be enough to keep the metals in solution at pH 6-8.9. plate obtained and provide the desired appearance to the alloy deposit. Neutral baths may contain common chelating agents to keep the metal ions in

Brief Summary Text - BSTX (50);

To further enhance the corrosion resistance of the alloy deposit, small amounts of trace metals which will codeposit with the  $\frac{1}{2inc}$  alloy may be added to the electroyte. For example, soluble salts of chromium, titanium, tin, cadmium, or indium may be added to the bath in amounts of 5 mg/l to 4 g/l.

Brief Summary Text - BSTX (61);

maintain an effective amount of the metal ions in solution. The preferred chelating or complexing agents are citric acid, gluconic acid, glucoheptanoic acid, tertaric acid, acoopic acid, isosacochic acid, malic acid, glutaric acid, mulconic acid, glutamic acid, amonium, appartic acid, and the like as well as their alkali metal, ammonium, zinc or ferrous salts thereof.

Additionally, suitable complexing or chelating agents that can be employed include nittilo triacetic acid, ethylene diamine tetraethanol and ethylene ដុ The zinc-iron alloy electroplating bath can range in pH from about 0 up about 6.5, preferably from about 0.5 to about 5. When the bath is weekly acidic or near neutral, such as at a pH of about 3 to about 6.5, it is preferred to incorporate conventional complexing or chelating agents to diamine tetra acetic acid and salts thereof. 

Current US Original Classification - CCOR (1):

Current US Cross Reference Classification - CCXR (1):  $\frac{205/245}{}$ 

Patent Number: Date of Patent: 2 E United States Patent Martin et al.

4,717,458 Jan. 5, 1988

[54] ZINC AND ZINC ALLOY ELECTROLYTE AND PROCESS

Inventors: Sylvia Martin, Utica; Roy W. Herr, Troy; Wather J. Whocsentak, Utica; Alte M. Strom, Warren, all of Mich. E

Assignee E

Appl. No.: 920,636 [2]

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4,397,718 6/1983 Martin 4,401,526 6/1983 Martin 4,444,629 4/1984 Martin et al. ...

204/35 Y 204/44.2 204/44.2 204/44.2

OMI International Corporation, Warren, Mich.

...... CASD 3/22; C25D 3/56 204/44.5 204/44.5 Oct. 28, 1986 Lis Q. 温泉

An aqueous bath suitable for electrodepositing sine and alloys of sine including sine-nickel, zine-cobelt, zine-nickel-cotalt, zine-tron-nickel-cotalt, zine-tron-nickel-cotalt, zine-tron-

Primary Examiner—G. L. Kaplan Attornes, Agent, or Firm—Richard P. Mueller

ABSTRACT

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ening amount of an AABB-type polyamids brightener in an amount effective to produce an electrodeposit of

cobalt, and zinc-nickel-cobalt-iron containing a bright-

the desired brightness. The invention further contem-plates the process of electrodepositing aim said since alloys of the foregoing types on a conductive substrate employing the aqueous electrolyne.

204/55 R, 55 Y, 44.2, 204/44.5, 114, 123

U.S. PATENT DOCUMENTS 3,454,475 7/1969 Rushmere et al ...... References Cited

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28 Claffins, No Drawings

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Brief Summary Text - BSTX (2):

The difficulties associated with the consistent electrodeposition of bright, conventional chromium deposits coupled with the imposition of government conventional chromium deposits coupled with the imposition of government restrictions on the discharge of toxic effluents including hazavalent chromium present in conventional chromium electroplating baths has prompted the development of alternative electroplating bath compositions and techiques for depositing metal alloys incended to duplicate the color and characteristics of conventional chromium deposits. In U.S. Pat. No. 3891,919, for exaple, an electroplating bath is disclosed for depositing a ternary alloy consisting of cohalt and zinc which simulates a chromium deposit. In U.S. Pat. No. 4,035,249 which is assigned to the same assignee as the present invention, an electroplating bath composition is disclosed for depositing a binary alloy consisting of cobalt and tin. The bath composition and process as disclosed in the last mentioned U.S. patent is primarily adapted for the bulk plating of small workpaces such as in barrels and some difficulty has been encountered in adapting the bath for rack plating of workpieces.

Brief Summary Text - BSTX (7):

The complexing agent preferably comprises citric acid including the alkali metal, ammonium, zinc and cobalt salts thereof. Gluconic acid, alpha glucohaptonic acid, tertaric acid, sa well as the alkali metal, ammonium, zinc, and cobalt salts thereof, can also be amployed preferably in combination with at least 10% of the citric acid complexing compound.

Brief Summary Text - BSTX (15):

In addition to the cobalt and zinc ions, the electrolyte contains a controlled amount of an organic complexing agent present to maintain substantially all of the cobalt and zinc ions in solution. Complexing egents which have been found suitable in accordance with the practice of the present invention include circuic acid, gluconic acid, all as the alkali metal.

Textaric acid, as well as the alkali metal amonium, zinc, cobalt salts thereof. Of the foregoing, citric acid or the citric acid salts constitutes the preferred material. The use of citric acid and/or a citrate salt constitutes the preferred practice for electrodepositing a cobalt-zinc alloy employing rack plating techniques. On the other hand, sodium glucoheptonate spensis to provide the best results when the bath is employed for bulk plating of workpieces in an electroplating barrel. The use of the alternative complexing agents and/or the salts thereof for rack plating have been found suitable for electrodepositing a cobalt-zinc alloy at a plating thickness less than about 0.1 mil. However, when electroplating the cobalt-zinc alloy in mounts greater than 0.1 mil, such alternative complexing agent in an amount of at least about 5 to 10 g/l in the alectrolyte provides satisfactory electrodepositis of a clattac acid or a citrate salt in combination with the alternative complexing agent in an amount of at least about 5 to 10 g/l in the thickness. Por the reack plating of conductive substrates employing the most preferred conditions as hereinable of escribed, cittic acid or a citrate complexing agent in an amount of an electrolyte provides satisfactory electrodeposits of a relatively high preferred conditions as hereinable or electrodeposits of a relatively in an amount of about 40 g/l has been found most desirable.

Brief Summary Text - BSTX (16):

The concentration of the complexing agent in the electrolyte may range from

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4,299,671 Nov. 10, 1981

BATH COMPOSITION AND METHOD FOR ELECTRODEPOSITING COBALLYZING LACOYS SIMULATING A CHROMUM PLATING

Inventors: Robert A. Tremmel, Woodhaven; Walter J. Wieczerniak, Uricz, both of E

Assignee: Hooker Chemicals & Plastics Curp., Warren, Mich.

Jun. 13, 1980 Appl. No.: 159,402 温泉 

204/35 R, 38 References Cited

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Primary Examiner—G. L. Kaplan Anorney, Agent, or Firm-Richard P. Mueller

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FOREIGN PATENT DOCUMENTS

254296 10/1969 U.S.B.R.

4,033,249 7/1977 Winozerniak

ABSTRACT

A bath composition and method for electrodepositing a cobalt-aire, alloy an a conductive substrate which gains lates the appearance of a conventional elementim electrodeposit. The bath comprises an aqueous solution having a pH of about 6 to about 9 constituting a controller fartie of cobalt time and fair tons and a complexing agent sufficient to mixture the cobalt and a complexing agent sufficient to mixture the cobalt and after loss in solution. The bath and incertoed are particularly adapted. able for rack plating articles to impart a deconsive bright chromium-like appearance and semi-bright de-posits simulating conventional chromium platings.

40 Outrage No Drawings ASIAN [ ] G B D . | Birdon M. | A Explorago | O Changes | B 1004 pto | B 1001870. 